

ACID PRECIPITATION IN
METROPOLITAN TORONTO AND
ADJACENT URBAN CENTERS

Repl. # 1868

METRIC CONVERSION TABLES

INCHES TO MILLIMETRES

mm	In.	mm	In.	mm	In.	mm	In.
254.000	1	25.400	0.1	2.540	0.01	0.254	0.001
508.000	2	50.800	0.2	5.080	0.02	0.508	0.002
762.000	3	76.200	0.3	7.620	0.03	0.762	0.003
1016.000	4	101.600	0.4	10.160	0.04	1.016	0.004
1270.000	5	127.000	0.5	12.700	0.05	1.270	0.005
1524.000	6	152.400	0.6	15.240	0.06	1.524	0.006
1778.000	7	177.800	0.7	17.780	0.07	1.778	0.007
2032.000	8	203.200	0.8	20.320	0.08	2.032	0.008
2286.000	9	228.600	0.9	22.860	0.09	2.286	0.009
2540.000	10	254.000	1.0	25.400	0.10	2.540	0.010

FRACTIONAL INCH TO MILLIMETRES

mm	In.	mm	In.	mm	In.	mm	In.
0.397	$\frac{1}{16}$	6.747	$\frac{1}{8}$	13.097	$\frac{1}{4}$	19.447	$\frac{3}{8}$
0.794	$\frac{1}{8}$	7.144	$\frac{3}{16}$	13.494	$\frac{1}{2}$	19.844	$\frac{7}{8}$
1.191	$\frac{3}{16}$	7.541	$\frac{1}{4}$	13.891	$\frac{3}{8}$	20.241	$\frac{1}{2}$
1.588	$\frac{1}{4}$	7.938	$\frac{5}{16}$	14.288	$\frac{1}{2}$	20.638	$\frac{5}{8}$
1.984	$\frac{5}{16}$	8.334	$\frac{3}{8}$	14.684	$\frac{3}{4}$	21.034	$\frac{1}{2}$
2.381	$\frac{3}{8}$	8.731	$\frac{1}{2}$	15.081	$\frac{5}{8}$	21.431	$\frac{3}{4}$
2.778	$\frac{1}{2}$	9.128	$\frac{5}{8}$	15.478	$\frac{3}{4}$	21.828	$\frac{7}{8}$
3.175	$\frac{5}{8}$	9.525	$\frac{3}{4}$	15.875	$\frac{7}{8}$	22.225	$\frac{1}{2}$
3.572	$\frac{3}{4}$	9.922	$\frac{7}{8}$	16.272	$\frac{1}{2}$	22.622	$\frac{5}{8}$
3.969	$\frac{7}{8}$	10.319	$\frac{1}{2}$	16.669	$\frac{1}{4}$	23.019	$\frac{1}{8}$
4.366	$\frac{1}{2}$	10.716	$\frac{1}{4}$	17.066	$\frac{1}{8}$	23.416	$\frac{1}{16}$
4.762	$\frac{1}{4}$	11.112	$\frac{1}{8}$	17.462	$\frac{1}{16}$	23.812	$\frac{1}{32}$
5.159	$\frac{1}{8}$	11.509	$\frac{1}{16}$	17.859	$\frac{1}{32}$	24.209	$\frac{1}{64}$
5.556	$\frac{1}{16}$	11.906	$\frac{1}{32}$	18.256	$\frac{1}{64}$	24.606	$\frac{1}{128}$
5.953	$\frac{1}{32}$	12.303	$\frac{1}{64}$	18.653	$\frac{1}{128}$	25.003	$\frac{1}{256}$
6.350	$\frac{1}{64}$	12.700	$\frac{1}{128}$	19.050	$\frac{1}{256}$	25.400	$\frac{1}{512}$

FEET TO METRES (1 ft. = 0.304801 m)

Metres	Ft.	Metres	Ft.	Metres	Ft.	Metres	Ft.
30.480	100	3.048	10	0.305	1	0.030	0.1
60.960	200	6.096	20	0.610	2	0.061	0.2
91.440	300	9.144	30	0.914	3	0.091	0.3
121.920	400	12.192	40	1.219	4	0.122	0.4
152.400	500	15.240	50	1.524	5	0.152	0.5
182.880	600	18.288	60	1.829	6	0.183	0.6
213.361	700	21.336	70	2.134	7	0.213	0.7
243.841	800	24.384	80	2.438	8	0.244	0.8
274.321	900	27.432	90	2.743	9	0.274	0.9
304.801	1000	30.480	100	3.048	10	0.305	0.10

MILES TO KILOMETRES (1 mile = 1.609347 km)

km	Miles	km	Miles	km	Miles	km	Miles
1,609.35	1000	160.93	100	16.09	10	1.61	1
3,218.69	2000	321.87	200	32.19	20	3.22	2
4,828.04	3000	482.80	300	48.28	30	4.83	3
6,437.39	4000	643.74	400	64.37	40	6.44	4
8,046.74	5000	804.67	500	80.47	50	8.05	5
9,656.08	6000	965.61	600	96.56	60	9.66	6
11,265.43	7000	1,126.54	700	112.65	70	11.27	7
12,874.78	8000	1,287.48	800	128.75	80	12.87	8
14,484.12	9000	1,448.41	900	144.84	90	14.48	9
16,093.47	10,000	1,609.35	1000	160.93	100	16.09	10

WEIGHT/MASS

1 GRAM	= 1000 MILLIGRAMS = 15.432 GRAINS
1 KILOGRAM	= 1000 GRAMS = 2.2046 POUNDS
1 METRIC TON	= 1000 KILOGRAMS = 2204.6 POUNDS
1 GRAIN	= 0.0648 GRAM
1 OUNCE	= 28.35 GRAMS
1 POUND	= 453.6 GRAMS
1 TON	= 907.2 KILOGRAMS

FORMULAS

1 LITRE	= 1000 CU. CENTIMETRES = 1.05 QUART
1 IMPERIAL QUART	= 1.1366 LITRES
1 IMPERIAL GALLON	= 4.5461 LITRES
1 US QUART	= 0.946 LITRE
1 US GALLON	= 3.785 LITRES

MILLIMETRES TO INCHES

mm	In.	mm	In.	mm	In.	mm	In.
100	3.9370	10	0.3937	1	0.0394	0.1	0.0039
200	7.8740	20	0.7874	2	0.0787	0.2	0.0079
300	11.8110	30	1.1811	3	0.1181	0.3	0.0118
400	15.7480	40	1.5748	4	0.1575	0.4	0.0157
500	19.6850	50	1.9685	5	0.1968	0.5	0.0197
600	23.6220	60	2.3622	6	0.2362	0.6	0.0236
700	27.5591	70	2.7559	7	0.2756	0.7	0.0276
800	31.4961	80	3.1496	8	0.3150	0.8	0.0315
900	35.4331	90	3.5433	9	0.3543	0.9	0.0354
1,000	39.3701	100	3.9370	10	0.3937	1.0	0.0394

FEET TO MILLIMETRES

Ft.	mm	Ft.	mm	Ft.	mm	Ft.	mm
100	30,480	10	3,048	1	304.8	0.1	30.48
200	60,960	20	6,096	2	609.6	0.2	60.96
300	91,440	30	9,144	3	914.4	0.3	91.44
400	121,920	40	12,192	4	1,219.2	0.4	121.92
500	152,400	50	15,240	5	1,524.0	0.5	152.40
600	182,880	60	18,288	6	1,828.8	0.6	182.88
700	213,360	70	21,336	7	2,133.6	0.7	213.36
800	243,840	80	24,384	8	2,438.4	0.8	243.84
900	274,320	90	27,432	9	2,743.2	0.9	274.32
1,000	304,800	100	30,480	10	3,048.0	1.0	304.80

METRES TO FEET (1 m = 3.280833 ft.)

Metres	Ft.	Metres	Ft.	Metres	Ft.	Metres	Ft.
100	328.083	10	32.808	1	3.281	0.1	0.328
200	656.167	20	65.617	2	6.562	0.2	0.656
300	984.250	30	98.425	3	9.842	0.3	0.984
400	1,312.333	40	131.233	4	13.123	0.4	1.312
500	1,640.416	50	164.042	5	16.404	0.5	1.640
600	1,968.500	60	196.850	6	19.685	0.6	1.968
700	2,296.583	70	229.658	7	22.966	0.7	2.297
800	2,624.667	80	262.467	8	26.247	0.8	2.625
900	2,952.750	90	295.275	9	29.528	0.9	2.953
1,000	3,280.833	100	328.083	10	32.808	1.0	3.281

KILOMETRES TO MILES (1 km = 0.621370 mile)

km	Miles	km	Miles	km	Miles	km	Miles
1,000	0.62137	100	0.6214	10	0.621	1	0.62
2,000	1.24274	200	124.27	20	12.43	2	1.24
3,000	1.86411	300	186.41	30	18.64	3	1.86
4,000	2.48548	400	248.55	40	24.86	4	2.49
5,000	3.10685	500	310.68	50	31.07	5	3.11
6,000	3.72822	600	372.82	60	37.28	6	3.73
7,000	4.34959	700	434.96	70	43.50	7	4.35
8,000	4.97096	800	497.10	80	49.71	8	4.97
9,000	5.59233	900	559.23	90	55.92	9	5.59
10,000	6.21370	1,000	621.37	100	62.14	10	6.21

TEMPERATURE

(Degrees)	CELSIUS	FAHRENHEIT
	(formerly Centigrade)	
-273.2	=	-459.7
-40	=	-40
-17.7	=	0
0	=	+32
+37	=	+98.6
+100	=	+212

LIQUIDS

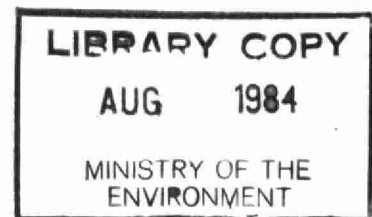
FAHRENHEIT: 9 x DEGREES C	+32
CELSIUS: 5 x (DEGREES FAHR. -32)	9

ACID PRECIPITATION IN METROPOLITAN TORONTO
AND ADJACENT URBAN CENTERS

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CENTRAL REGION



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SUMMARY AND CONCLUSIONS

Precipitation in Metropolitan Toronto was weakly acidic during the period 1956-1958, with grand means in the range of pH 5.3-5.6. Acidity was higher during winter, and correlated significantly with sulphate concentration in precipitation. Limited data at 67 College Street, Toronto during 1960-1966 indicated similar seasonal trends. However, precipitation at this site became more rapidly acidified than expected, and annual pH varied from 4.1 to 4.4. In spite of these differences, it is sufficient to say that precipitation in Toronto was already acidic during 1956-1966. Local sulphur dioxide emissions from Hearn Generating Station and industrial sources along Lakeshore was considered relatively more important in causing the acidification of precipitation.

Recent measurements during November 1976 - August 1977 indicated widespread areas in Metropolitan Toronto being affected by acid precipitation. Grand means below pH 4.5 were measured at monitoring stations located in areas bounded by Sheppard Avenue, McCowan Road, College and Dufferin Streets. An equally acidic zone was found in parts of Etobicoke and Mississauga just north of Lakeview Generating Station. In contrast to the historical data, recent measurements indicated that precipitation was more acidic during summer, and particularly August 1977 when an episode occurred. Moderately acidic precipitation was detected uniformly across Metropolitan Toronto and adjacent urban centers along upper Lake Ontario during that month, with mean pH in the range of 3.6-4.8.

Regardless of the locations of monitoring stations with respect to Lakeview Generating Station, the pH of precipitation decreased significantly with the hours of SW or S winds. Significant positive correlations with northerly winds were generally observed. Such a strong dependence of the acidity of precipitation on southerly flows appeared to favour the current hypothesis of regional transport of sulphur oxides, acid sulphates and other acidic pollutants dispersed from tall stacks in remote urban centers.

A simple model was set up to predict annual pH changes of waters in lakes associated with estimated annual acid input of approximately 60-100 mg. eq. H^+ /sq. meter via wet and dry depositions. Calculations were performed for Lake Ontario, Lake Simcoe, and fifteen lakes in Haliburton-Muskoka region. The results indicated small pH decreases (about 0.02-0.07 pH unit per year) for waters in Lake Ontario and Lake Simcoe, reflecting their good buffering capacities. Even if the acid loading were tripled from the current estimate, the pH of waters in both lakes would not fall below 7 after two decades. However the pH of waters in Blue Chalk, Red Chalk, Jerry, Harp, Basshaunt, Solitaire, Little Clear and Buck Lakes would fall below 5 after 10-15 years at the current rate of airborne acid loading. Bigwind, Crosson, Gullfeather, Walker and Dickie Lakes would be more rapidly acidified; and reach critically acidic conditions within 3-7 years. Should the acid loading increase as a result of increased sulphur and nitrogen oxides emissions due to increased use of coal, acidification of these shallow, poorly-buffered lakes in Haliburton-Muskoka region would occur faster than expected.

The potential impacts of acid precipitation on mercury pollution in water was discussed. It follows from equilibrium and adsorption considerations that free mercuric ion concentration would increase enormously, perhaps by several orders of magnitude, in lakes with acidified waters and low chloride levels. Since the rate of mercury methylation in both aquatic and terrestrial systems depends on the availability of free mercuric ion, conditions in acidified lakes would become progressively favourable, and eventually optimum for enhanced methylation rate of mercury as a result of continued depositions of airborne acids and mercury through precipitation. Prevalence of methylmercury in the environment would conceivably result in rapid rise of mercury levels in fish, and hence a higher level of risk of methylmercury poisoning for men via food chain and other significant routes.

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I INTRODUCTION

Acid Precipitation and its effects on ecosystems is a matter of growing concern particularly in the industrialized countries of northern hemisphere (Ref. 1-2). The identified or suspected effects include acidification of lakes and streams, and resulting extinction of many species of fishes (Ref. 3-8, 10, 14); changes in the communities of microdecomposers, algae, aquatic macrophytes, zooplankton and zoobenthos (Ref. 9-13); acidification of soil and increased leaching of soil cations (Ref. 15, 16); increased leaching of nutrients from foliage, disruption of leaf physiology (Ref. 17) and reduced forest growth (Ref. 18). Acid rain and snow significantly below the normal pH value of 5.6 have been reported in Scandinavia, eastern and northeastern United States (Ref. 19-21), Sudbury and northeastern Ontario (Ref. 22, 23), and more recently in Muskoka, Haliburton, Parry Sound and Nipissing region (Ref. 24). This report presents the current measurements of acidic precipitation in Metropolitan Toronto, and the changes in acidity over the last two decades. Measurements were also extended to adjacent urban centres such as Oakville, Mississauga, Richmond Hill, Markham, New Market, Barrie, Collingwood, Bowmanville, Peterborough and Port Hope.

The first investigation of acid precipitation was conducted during 1956-1958 by Dr. Fisher, School of Hygiene, University of Toronto (Ref.

25). Monthly bulk precipitation samples were collected by means of "Toronto Bowls" (Ref. 36), and analyzed for free acidity (i.e. pH), sulphate and ammonium concentrations. Measurements of sulphur dioxide, soiling of particulate matter, and dust fallout were also carried out to determine the extent of air pollution in Toronto. The study was supported in part by a grant from the Commissioner of Property, City of Toronto; and initiated in July, 1954 at the suggestion of the Air Pollution Advisory Board, City of Toronto. Due to the lack of general interests in acid precipitation, routine measurements had been discontinued until October, 1976. Since then, ambient pH values of monthly bulk (wet and dry) precipitation samples have been measured in Metropolitan Toronto and adjacent urban centres.

In addition to those historical data collected by Fisher, limited data obtained during 1960-1966 are also available at our long term air monitoring station in downtown Toronto (station 31001, 67 College Street).

II METHOD

Bulk precipitation samples were collected by exposing polyethylene buckets (12" tall and 6" diameter) in the atmosphere over 30-day periods. Insoluble solids were filtered off, and the pH of clear liquids were measured by a calibrated pH meter and glass-electrode assembly at Air Quality Laboratory. The pH data reported were the final pH values measured.

It is well recognized that current researchers are in favour of the wet-only, event precipitation samples more than the monthly bulk (wet and dry) samples (Ref. 26). The latter may undergo chemical changes during the sampling period, and fallout of dust can possibly change the acidity and composition. Meteorological interpretations are usually more difficult since the effects of several precipitation events are combined. On the other hand, monthly bulk precipitation samples are more attractive in view of the relative ease of routine operations of combined dustfall/ precipitation stations, particularly when general constraints due to limited capacities and resources are experienced. An important question to wonder is to what extent would the interpretation and finding of acidity measurements be jeopardized at the sacrifice of data accuracy.

Kadlecak and Mohnen studied the time dependence of pH of rain (Ref. 27), which could be corre-

lated with the surface wind trajectories terminating at Schenectady, New York. The pH remained constant if the trajectories were from the south, but gradually increased by about 1/6 to 1/5 in a few hours if they came from the north, west and east across the southern Adirondack Mountains and southern Massachusetts. If the trajectories proceeded from the west along the Mohawk Valley, the pH gradually increased by about 1/3 in 2 to 4 days.

Dillon (Ref. 24) recently measured the pH of both bulk and event precipitation samples in south central Ontario. For those eight stations located on Precambrian Shield underlain by granitic rock, the mean pH readings of the bulk samples were lower than those of the event samples, with differences in the range of 0.03 to 0.21 pH unit. However, the converse was true for the three stations located off the Shield near Paleozoic region, which consists mainly of clastic and carbonate sediments. The mean pH readings of the bulk samples were higher than those of event samples by approximately 0.36 to 1.4 pH unit.

Keeping these studies of Kadlecsek and Dillon in mind, and recognizing the near neutrality or slight alkalinity (pH 6.8 - 7.4) of soils with some buffering capacity in southern Ontario (Ref. 28); our pH data of bulk precipitation samples in the study areas are expected to be underestimated values, but are indicative of the acid precipitation problem if they were

reported below pH 5.6. The interpretations would be more difficult if they were higher than pH 5.6. In general, the bulk precipitation samples should be more acidic than indicated by the measured pH. Hence the sacrifice of data accuracy at the expense of collecting monthly bulk precipitation samples would not obscure the true finding if the precipitation is strongly acidic, unless the stations are located near certain industries such as cement plants and stone quarries where fallout of alkaline dust can severely contaminate the precipitation samples.

The use of bulk samples also permits the evaluation of total acid fallout via wet and dry depositions. According to the study of sulphur cycle by Kellogg (Ref. 29), plant uptake and dry deposition account for 15% (75 million tons as sulphate per year) of total sulphur deposited per year on the global basis. Using a regional scale model of atmospheric sulphur pollution developed for the northeastern United States, Sheih (Ref. 30) showed that about 26% of the total sulphur emitted from 53 major power plants is deposited to the ground via dry deposition. These studies indicate that dry deposition of airborne sulphur compounds and other acidic pollutants cannot be neglected in the assessment of acid loadings on aquatic and terrestrial systems through precipitation.

In the context of this report, mean pH refers to the negative logarithm of arithmetic mean hydrogen ion concentration.

III RESULTS AND DISCUSSION

(i) Acidity of Precipitation during 1956-1958

A brief statistical summary of pH data of monthly bulk precipitation samples in Metropolitan Toronto during February, 1956 - June, 1958 is presented in Table 1. Mean pH values, calculated as the negative logarithms of arithmetic mean hydrogen ion concentrations, were in the range of 5.2 to 6.0; and minimum pH varied from 4.1 to 5.1. The pH isopleth plot is shown in Figure 1. It appears that slight acidification of precipitation in the City of Toronto and East York started before 1956. Hearn Generating Station was then the largest single source of local sulphur dioxide emissions. Maximum hourly sulphur dioxide concentrations were typically 0.5 - 0.8 ppm in the City, while the mean concentrations were 0.2 - 0.3 ppm.

Precipitation was generally more acidic during the winter or heating season, reflecting perhaps the influences of local sulphur dioxide emissions from Hearn Generating Station and industrial sources along the lakeshore. Sulphate concentrations were similarly higher during the winter. Significant inverse relationships between pH and sulphate in precipitation were observed at those stations where precipitation was relatively more acidic (Table 2).

(ii) Acidity of Precipitation during 1960-1966

Acid precipitation data are scarce between 1958 and 1976. Only six years of data (1960-1966) are available at our long term air monitoring station (67 College Street, Station 31001) in downtown Toronto. Table 3 shows a brief statistical summary of the pH data. Annual pH varied from 4.1 to 4.4 (Figure 2), with minimum pH in the range of 3.5 - 3.9. It is not understood why the precipitation was so rapidly acidified sometime between 1958 and 1960 in the City, and became more acidic by a factor of ten. Cogbill and Likens (Ref. 31) have shown that it is possible to compute the pH of chemically analyzed rainwater samples with reasonable accuracy, by means of a stoichiometric balance between cations and anions. Tests have shown that the pH of precipitation samples can be predicted within ± 0.1 unit. Accordingly, they constructed a map of average pH of precipitation predicted over the eastern United States during the period 1965-1966 (Fig. 3), based on the chemical data of Lodge (Ref. 32), Gambell and Fisher (Ref. 33). Extrapolation of contour lines to Toronto would give a predicted pH of 4.5, which agrees reasonably well with a grand mean of pH 4.3 measured at 67 College Street during the period 1960-1966.

A similar map was also constructed by Cogbill and Likens for eastern United States during the period 1955-1956 (Figure 4), based on the chemical data of Junge (Ref. 34, 35). However the extrapolated pH of 4.45 for Toronto was significantly lower than the measured values (pH 5.3 - 5.6). Unless the predicted pH values based on the chemical contents of U.S. rainwater samples are not precise enough to allow an extrapolation across the border to Toronto, our historical data might have been underestimated due to either the use of "Toronto Bowls" as collectors (Ref. 25, 36) by Fisher or the greater acid-neutralizing capacities of local dust particles before 1960. No definite conclusion can be drawn. However it is sufficient to say that the precipitation in Toronto was already acidic (below pH 5.6) during the period 1956-1966.

Similar to those early data obtained by Fisher during the period 1956-1958, the precipitation at 67 College Street, Toronto during the period 1960-1966 was most acidic in winter, particularly the November month.

Annual sulphur dioxide concentrations at the same site were 0.089 and 0.098 ppm respectively in 1965 and 1966. Annual sulphation rates measured by lead peroxide

candle were 2.16 - 2.95 mg. SO_3 /100 sq.cm./

day during 1962-1966, with maxima in the range of 3.33 - 4.58 mg SO_3 /100 sq.cm./day.

(iii) Acidity of Precipitation during November 1976 - August 1977

A series of pollution abatement programs have been implemented since the late sixties to control local sulphur dioxide and particulate emissions. With the conversions of Hearn Generating Station, Toronto Terminal Railways, Toronto General Hospital and Goodyear Tire, and the restrictions on sulphur contents of fuels; ambient sulphur dioxide levels have continuously declined throughout Metropolitan Toronto. The Ontario Annual Criterion of 0.02 ppm for sulphur dioxide has been met since 1973. Figures 5 and 6 show that both sulphur dioxide and sulphation levels measured at 67 College Street, Toronto have decreased by a factor of 5 since 1966. A corresponding decrease in the acidity of precipitation is expected at the first thought. Recent pH measurements of monthly bulk precipitation samples at the same site during November, 1976 - August, 1977 yield a mean of pH 4.9, and a range of 4.1 to 7.5. This decrease in acidity of precipitation over the last decade (by a factor of 3) is slightly smaller than the decline of sulphur dioxide concentration over the same period.

Acidity measurements of precipitation samples have been extended to other stations in Metropolitan Toronto and adjacent urban centers in the Region. A brief statistical summary of pH data is presented in Table 4. A map of pH isopleth plot is shown in Figure 7. The areas where acid precipitation had been detected were widespread, extending from Mississauga to Scarborough, and perhaps Pickering. Mean pH values below 4.5 were measured at stations located in areas bounded by Sheppard Avenue, McCowan Road, College and Dufferin Streets. An equally "acidic" zone was found in parts of Etobicoke and Mississauga just north of Lakeview Generating Station, the largest single source of sulphur dioxide emissions in Metropolitan Toronto today. As discussed earlier, our pH data were underestimates of real events. The precipitation samples should be more acidic than indicated by the measured pH values. Acidity measurements on samples collected at stations located along lake-shore were perhaps most underestimated, owing to contaminations by lake salts rich in calcium and magnesium.

(iv) Acid Precipitation Episode during
August 1977

The most striking differences between recent measurements and historical data (1956-1966) were the changes in seasonal

patterns of acid precipitation. In the past, precipitation was most acidic in winter and particularly the month of November. Recent measurements indicate that summer and especially August was the case. Figure 8 shows the widespread areas in Metropolitan Toronto receiving very acidic precipitation (less than pH 4) during August, 1977. Values lower than pH 3.5 were measured at some stations. This phenomenon was also uniformly observed across the urban centers along upper Lake Ontario (Figure 9), with mean pH in the range of 3.6 to 4.8 (Table 5). With local sulphur dioxide emissions well under control, the long-range transport of sulphur oxides and acidic pollutants from remote areas of anthropogenic emissions may play a relatively more important role in causing this acid-precipitation episode. Movement of warm, moist tropical air from the Gulf of Mexico over major urban centres into southern Ontario, particularly in the summer, can potentially increase the acidity of precipitation. Occurrence of elevated levels of suspended acid sulphates and ozone, associated with southerly or southwesterly flows, had been observed in August, 1976 over widespread areas in southern Ontario (Ref.37-39). Our suspended sulphate data for August, 1977 are not available at this time for assessing the apparent cause-consequence relationship between suspended sulphates and acidity of precipitation.

(v) Wind Dependence of Acidity of Precipitation

Dependence of acidity of precipitation on wind directions at selected stations in Oakville, Mississauga and Metropolitan Toronto was examined by determining the Pearson or Spearman Rank correlation coefficients of pH with hours of winds, depending on the data base. Wind directions were taken from the measurements at second level of meteorological tower at Evans Avenue, Etobicoke (Station 35033). Wind rose constructed during November 1976 -August 1977 is shown in Figure 10. Correlation coefficients for eight sectors of winds for stations 44010 (Oakville), 46010, 46031 (Mississauga), 35014 (Etobicoke), 34001, 34007 (North York), 31005, 31014 (Toronto), and 33024 (Scarborough) are presented in the forms of bar charts (Figure 11-19). Regardless of the locations of stations with respect to Lakeview Generating Station, which is the single largest source of local sulphur dioxide emissions; the pH of precipitation decreased significantly with the hours of SW or S winds. Significant positive correlations of the pH of precipitation with northerly winds were generally observed, suggesting the "alkaline" nature of northerly flows. Such a strong dependence of the acidity of precipitation on southerly flows appears to favor the hypothesis of regional

transport of sulphur oxides, acid sulphates and other acidic pollutants from remote urban centers. Figures 20 and 21 show the geographical distribution of power plant generating capacity and of total sulphur dioxide emission density upwind of the Great Lakes.

(vi) Acid Fallout

Total acid fallout via wet and dry depositions can be calculated by multiplying the hydrogen ion concentration (in milligram - equivalent per litre) with volume of bulk precipitation collected (in litre), and expressed in unit of mg. eq. H^+ ion per square metre per 30 days after taking into account the opening (6 in. diameter) of collector. Figure 22 shows the variations of ambient pH of bulk precipitation samples, and acid fallout at station 31014 (Spadina/Newhaven Drive, Toronto); where most acidic precipitation (pH 3.6-4.3) was detected throughout the monitoring period. Mean acid fallout was 5.2 mg. eq. H^+ /sq.m/30 days, with reported range of 0.7 - 13.7 mg. eq. H^+ /sq.m/30 days. Peak values of 13.7 and 10.0 mg. eq. H^+ /sq.m/30 days were measured in August and April respectively.

Total acid fallout was, in general, higher in summer than in winter presumably due to frequent summer rains (Fig. 23) and elevated levels of acid sulphates associated with

regional southerly flows. Figures 24 and 25 illustrate the seasonal variations of suspended sulphates, sulphur dioxide, sulphation rate and ozone concentrations at stations 31001 (67 College Street, Toronto), and 33003 (Lawrence/ Kennedy, Scarborough).

There is some evidence to support the hypothesis of Likens and Bormann (Ref.21) that acidification of precipitation is a consequence of the decrease in alkaline fly ash emissions from coal - burning plants subsequent to the installation of electrostatic precipitations, in combination with increasing emissions of sulphur oxides and nitrogen oxides. Figure 26 shows the continuous declines in fallouts of calcium and magnesium dusts at 67 College Street, Toronto (Station 31001) since 1973. Long-term decreases of total dust fallout, total suspended particulate, and soiling index of suspended particulate matter are presented in Figure 27.

Measurements of total acid fallout suggest an annual acid input of approximately 60-100 mg. eq.H⁺/sq.m into the aquatic and terrestrial systems via wet and dry depositions. It would be of interest to examine the resulting water quality changes in lakes, rivers and streams. Unfortunately historical and current data on pH, total alkalinity and

sulphate are usually limited to allow trend analysis and project changes in the future. The most interesting trend observed (Fig. 28) is the increase of sulphate concentration in Lake Ontario from 15 mg/l prior to 1910 (Ref. 40), to about 28 mg/l in 1972 (Ref. 41). This increase may be related to the combined effects of increased industrial waste discharges and increased loadings of airborne acid sulphates into the lake basin.

Significant changes in pH and total alkalinity of waters in well-buffered lakes located in the limestone region south of the Precambrian Shield are not expected to occur in very near future. Both Lake Ontario and Lake Simcoe waters, for example, have total alkalinity of approximately 100 mg/l as calcium carbonate, and pH above 8 (Ref. 41, 42). However continued and increased loadings of airborne acids into the basins would conceivably result in gradual declines in total alkalinity and pH. The impacts should be greater on poorly-buffered lakes located in Precambrian Shield underlain by granitic rocks (Ref. 43, 44). Significant decline in buffering capacity in Walker Lake between 1971 and 1976 has been noted recently (Ref. 24).

(vii) Prediction of pH Changes of Lake Waters

Annual pH changes of lake waters associated with different loadings of airborne acids into the basins can be calculated from current pH and total alkalinity data. The assumptions involved are:

- (a) The water is unsaturated with respect to calcium carbonate,
- (b) Total alkalinity is established by the concentrations of bicarbonate, carbonate and hydroxide ions,
- (c) Strong mineral acids are major hydrogen ion contributors to the acidity of precipitation.

Expressing all concentration terms in moles per litre, the total alkalinity (Alk) is

$$(\text{Alk}) = (\text{HCO}_3^-) + 2(\text{CO}_3^{--}) + (\text{OH}^-) - (\text{H}^+) \quad (1)$$

The total concentration of dissolved inorganic carbon species (C_T) is expressed by

$$(C_T) = (\text{H}_2\text{CO}_3^*) + (\text{HCO}_3^-) + (\text{CO}_3^{--}) \quad (2)$$

By using the equilibrium expressions (3)-(5) at 25°C,

$$(\text{H}^+) (\text{OH}^-) = K_w = 1 \times 10^{-14} \quad (3)$$

$$(\text{H}^+) (\text{HCO}_3^-) / (\text{H}_2\text{CO}_3^*) = K_1 = 4.45 \times 10^{-7} \quad (4)$$

$$(\text{H}^+) (\text{CO}_3^{--}) / (\text{HCO}_3^-) = K_2 = 4.69 \times 10^{-11} \quad (5)$$

where K_1 and K_2 are the first and second dissociation constants of carbonic acid, equations (1) and (2) can be transformed to:

$$(\text{CO}_3^{=}) = [(\text{Alk}) + (\text{H}^+) - K_w/(\text{H}^+)]/[(\text{H}^+)/K_2 + 2] \quad (6)$$

$$(\text{C}_T) = (\text{CO}_3^{=})[(\text{H}^+)^2/K_1K_2 + (\text{H}^+)/K_2 + 1] \quad (7)$$

It is most convenient mathematically to define the buffer index, β , of water as

$$\beta = - \frac{d(\text{C}_A)}{dpH} \quad (8)$$

when the addition of $d\text{C}_A$ moles of strong acid to one litre of solution decreases its pH by an amount dpH . It can be shown from charge consideration that:

$$(\text{C}_A) = (\text{H}^+) + (\text{Alk}) - (\text{OH}^-) - (\text{HCO}_3^-) - 2(\text{CO}_3^{=})$$

Differentiating (C_A) with respect to (H^+) gives

$$\frac{d(\text{C}_A)}{d(\text{H}^+)} = 1 + \frac{K_w}{(\text{H}^+)^2} + \frac{K_1(\text{C}_T)}{[(\text{H}^+)^2 + K_1(\text{H}^+) + K_1K_2]^2} \left\{ \frac{(\text{H}^+)^2 + K_1K_2 + 4(\text{H}^+)K_2}{[(\text{H}^+)^2 + K_1(\text{H}^+) + K_1K_2]^2} \right\} \quad (9)$$

$$\begin{aligned} \text{Now } \beta &= - \frac{d(\text{C}_A)}{dpH} = - \frac{d(\text{C}_A)}{d(\text{H}^+)} \frac{d(\text{H}^+)}{dpH} \\ &= 2.303 \cdot (\text{H}^+) \frac{d(\text{C}_A)}{d(\text{H}^+)} \end{aligned} \quad (10)$$

Substituting (9) in (10) yields

$$\beta = 2.303 \left\{ (\text{H}^+) + \frac{K_w}{(\text{H}^+)} + \frac{K_1(\text{C}_T)(\text{H}^+)[(\text{H}^+)^2 + K_1K_2 + 4(\text{H}^+)K_2]}{[(\text{H}^+)^2 + K_1(\text{H}^+) + K_1K_2]^2} \right\} \quad (11)$$

If pH and total alkalinity of water are known, then the concentration terms, (CO_3^{--}) and (C_T) , can be calculated from equations (6) and (7); and buffer index, β , from equation (11).

To calculate the annual pH change of water associated with an acid input of Y moles H^+ per square meter per year, consider a surface water area of one square meter and a mean lake depth of D meters. The volume of lake water affected by acid input is

$$V = 10^3 D \text{ lit/sq. meter}$$

The annual pH change, ΔpH , resulting from the acid input of Y moles $\text{H}^+/\text{m}^2/\text{year}$ is given by

$$\Delta \text{pH} = - \frac{Y}{10^3 D} \cdot \frac{1}{\beta}$$

The annual pH of Lake water can be calculated from year to year by performing the computations for a number of cycles as desired. New pH and alkalinity values are used for each new cycle, where

$$\begin{aligned} (\text{pH})_N &= (\text{pH})_{N-1} + (\Delta \text{pH})_{N-1} \\ (\text{Alk})_N &= (\text{Alk})_{N-1} - \left(\frac{Y}{10^3 D} \right)_{N-1} \end{aligned}$$

and N denotes the number of cycles.

Calculations were performed for Lake Ontario, Lake Simcoe and fifteen lakes in Haliburton-Muskoka region. Year to year variations of annual pH of lake waters with different acid loadings are graphically presented in Figures 29-43. The calculated pH decreases would be small (about 0.02-0.07 pH unit per year) for waters in Lake Ontario and Lake Simcoe, reflecting their good buffering capacities. Even if the acid loading were tripled from the current estimate of 0.06 mole H^+ /sq.m/year, the pH of waters in both lakes would not fall below 7 after two decades.

In contrast to Lake Ontario and Lake Simcoe, many lakes in Haliburton-Muskoka region are shallow and poorly buffered. Current pH of lake waters fall between 6.0 and 6.5, with total alkalinity in the range of 5-10 mg/l as calcium carbonate (Ref. 24).

If the airborne acid loading were maintained at the current estimate of 0.06 mole H^+ /sq.m/year, our calculations indicate that the pH of waters in Blue Chalk, Red Chalk, Jerry, Harp, Basshaunt, Solitair, Little Clear and Buck Lakes (Fig. 31-38) would fall below 5 after 10-15 years. Bigwind, Crosson, Gullfeather, Walker and Dickie Lakes would be more rapidly acidified (Fig. 39-43); and reach critically acidic conditions within 3-7 years. The conditions would be most alarming for the last three lakes. Should the acid loadings increase from current estimate as a result of increased sulphur and nitrogen oxides emissions due to increased use of coal, acidification of these shallow, poorly-buffered lakes would occur faster than expected.

(viii) Potential Impacts of Acid Precipitation
on Heavy Metal Pollution in Water

Although the effects of acid stress on aquatic, forest and terrestrial systems have been well studied by current researchers, the area that lacks attention is the potential enhancement of adverse effects of heavy metals on fish and other aquatic organisms in acidified lakes, rivers and streams. The metal that causes greatest concern is mercury, in view of its natural occurrence, wide distributions and toxicities of its mono and dialkyls (Ref.45).

A variety of metal complexes can be formed in aquatic system. The equilibrium distributions of metal complexes and chemical composition of waters are governed by many important parameters, such as the pH of aqueous medium, the type and concentration of metals, complexing inorganic and organic ligands; and the redox environment of the system (Ref.46). Decreasing the pH and total ligand concentration would reduce the extent of metal complexation, and hence increase the availability of free (or uncomplexed) metal ions. As examples for illustration, Figure 44 shows that about 90% of total cobalt is uncomplexed at pH 5 in the cobalt (II) - histidine system, under the experimental conditions cited. As pH approaches 7, almost 99.9%

of cobalt ions become tied up in the forms of Co(Hist)^+ and Co(Hist)_2 complexes. Decreasing the total chloride level in mercuric-chloride system reduces the extents of formation of HgCl^+ , HgCl_2 , HgCl_3^- and HgCl_4^{--} complexes; and results in enormous increase in concentration of free mercuric ion (Fig. 45). The enhanced solubility of mercuric oxide in acidified water is shown in Figure 46, and a drop in pH from 8 to 5 would increase the concentration of free mercuric ion by six orders of magnitude. Adsorption of mercuric ion from aqueous solution onto silica increases abruptly above pH 2 (Fig. 47), reaches maximum between pH 4-6, and then decreases with increasing pH. It follows from equilibrium and adsorption considerations that free mercuric ion concentration would increase enormously, perhaps by several orders of magnitude, in lakes with acidified waters and low chloride levels.

The biologically significant form of mercury has been demonstrated to be methylmercury. Being soluble in water, it is taken up more readily than other forms of mercury by aquatic organisms. In common with many lipid-soluble substances, methylmercury is readily concentrated and stored in the tissues of fish and other aquatic organisms (Ref. 45). Inorganic mercury can be methylated through bacterial action under aerobic and anaerobic conditions.

Demethylation of methylmercury also occurs in nature, and hence the concentration of methylmercury in the environment depends on the combined reaction kinetics of methylation and demethylation processes.

The rates and extent of methylation are affected by many factors (Ref.47-49); among them are: availability of free mercuric ions, concentrations of total mercury input, pH, temperature, and growth rate or metabolic activity of methylating organisms. The first three factors are actually related through the various equilibria involved.

Both the kinetics and mechanism of this reaction are now understood in detail (Fig.48). According to Wood (Ref.50), the reaction involves an initial displacement of the base benzimidazole from the coordination sphere of cobalt atom to set up an equilibrium mixture of "base-on" and "base-off" methylcobalamin. This reaction is first order in free mercuric ion and in methylcobalamin (i.e. reaction rate increases linearly with increasing reactant concentrations). The equilibrium constant is 70 ± 5 in favour of the "base-off" species. The equilibrium is followed by electrophilic attack of free mercuric ion on both "base-on" and "base-off" methylcobalamin to give methylmercury as product, and both reactions are first order in free

mercuric ion. However the reaction with "base-on" molecule is 1,000 times faster than that with "base-off" molecule. Interaction of benzimidazole (B_z) with cobalt increases the electron density on the metal atom and facilitates the displacement of methyl group as CH_3^- . Methylmercuric ion can further react with methylcobalamin to give dimethylmercury as product, but this reaction is 6,000 times slower than the reaction with free mercuric ion. This is understandable as CH_3Hg^+ is less "electrophilic" than Hg^{2+} .

The first-order dependence of overall methylation rate on free mercuric concentration suggests the pH dependence from equilibrium and adsorption considerations. In fact the pH-rate profile of the methylation of "base-off" molecule is bell-shaped, with maximum rate at pH 4.5 (Ref.49). Recent study of abiological methylation of mercury in soil (Ref.51) also shows similar pH dependence of methylation rate, with maximum at pH 4.5.

It appears from the foregoing discussion that the conditions in acidified lakes and soils would become progressively favourable, and eventually optimum for enhanced methylation rate of mercury as a consequence of the depositions of airborne acids and mercury through precipitation. Prevalence of methylmercury in the environment would

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It appears from the foregoing discussion that the conditions in acidified lakes and soils would become progressively favourable, and eventually optimum for enhanced methylation rate of mercury as a consequence of the depositions of airborne acids and mercury through precipitation. Prevalence of methylmercury in the environment would

result in rapid rise of mercury level in fish, and hence a higher level of risk of methylmercury poisoning for men via food chain and other significant routes. Mercury concentrations in various fish species in many Ontario Lakes have already exceeded the safe level of 0.5 ppm for unrestricted human consumption (Ref. 52). It is most interesting to note that the mercury levels in fish in well-buffered Lake Ontario and Lake Simcoe have been classified in the A(0.5 ppm) and B(0.5-1.0 ppm) categories. However the fish samples caught in more acidic Buck Lake contained mercury levels in B, C(1.0-1.5 ppm) and D categories (1.5 ppm). As expected from theoretical consideration, there may be some relationship between the acidity of water and mercury level in fish.

In summary, acid precipitation is a complex, interdisciplinary environmental problem which can significantly influence the ecosystems at different levels. Ambient air quality standards and objectives have been traditionally established on the basis of direct effects of airborne contaminants on health, vegetation and materials. Protection of environment as a whole would be more adequate if the potential impacts of air pollutants on water quality, aquatic life and terrestrial system were also considered in standard setting.

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TABLE 1 pH Data of Monthly Bulk Precipitation Samples
in Metropolitan Toronto During February 1956-
June 1958

Location	# of Samples	Mean* pH	Range	# of Samples < pH 5.6
School of Hygiene U. of Toronto	26	5.3	4.1-7.0	4
269 Coxwell Avenue	28	5.3	4.2-7.0	8
35 Booth Avenue	28	5.6	4.8-7.1	5
Devenport/New Street	28	5.2	4.5-7.2	12
2721 Danforth Ave.	28	5.3	4.6-7.4	8
43 Junction Road	27	5.4	4.5-7.0	8
Steele/Dufferin	25	5.3	4.4-7.3	6
Keating Street	28	5.9	5.1-7.1	3
181 Fleet St.E.	28	5.7	4.9-7.0	5
95 Wellesley St.E.	28	5-3	4.5-7.1	10
Bowie Avenue	28	5.8	5.0-7.2	5
Weston Fire Dept.	28	5.9	4.9-7.5	2
615 Royal York Rd.S.	28	6.0	4.9-7.4	1
42 Hollinger Road	28	5.3	4.2-7.4	7
1609 Queen St.W	28	5.8	4.9-7.6	3
Strachan/Ordance	28	5.4	4.8-7.7	11
Devenport/Wineva	28	5.4	4.8-7.6	10
Yonge/Montgomery	27	5.4	4.8-7.4	9

* Mean pH calculated as the negative logarithm of the
arithmetic mean hydrogen ion concentration.

Table 2 Pearson Correlation of pH with Sulphate in
Precipitation (February 1956-June 1958)

Station	Corr. Coeff.	No. of Samples	Level of Significance
School of Hygiene, U. of Toronto	- 0.46	26	≤ 0.05
Devonpot/New Street	- 0.47	28	≤ 0.01
43 Junction Road	- 0.47	28	≤ 0.01
95 Wellesley E.	- 0.47	28	≤ 0.01
1609 Queen St.W	- 0.45	28	≤ 0.05
Strachan/Ordnance	- 0.52	28	≤ 0.01
Central Railway Yards John Street	- 0.66	17	≤ 0.01

Table 3 pH Data of Monthly Bulk Precipitation Samples
at 67, College Street, Toronto

Year	# of Samples	Annual pH*	Range	# of Samples < pH 5.6
1960	11	4.4	3.7-7.2	6
1961	12	4.2	3.5-6.7	9
1962	12	4.3	3.6-6.8	8
1963	12	4.3	3.6-6.9	7
1964	12	4.4	3.9-6.5	9
1965	12	4.1	3.6-7.0	9
1966	12	4.3	3.6-6.0	8

* Calculated as the negative logarithm of arithmetic mean hydrogen ion concentration.

Table 4 pH Data of Monthly Bulk Precipitation Samples
in Metropolitan Toronto and Adjacent Centers
during November, 1976 - August, 1977

Location	Station Number	No. of Samples	Mean* pH	Range	No. of Samples < pH 5.6
Toronto	31001	15	4.9	4.1 - 7.5	3
	31003	9	5.0	4.1 - 7.5	2
	31004	9	4.4	3.5 - 6.6	4
	31005	10	4.5	3.9 - 6.7	8
	31006	11	6.1	5.7 - 6.9	0
	31008	8	4.6	3.8 - 7.5	4
	31010	9	5.8	5.1 - 7.3	1
	31012	8	4.9	4.3 - 6.1	5
	31013	9	4.2	3.4 - 7.2	4
	31014	8	3.9	3.6 - 4.3	8
	31018				
	31050				
	31051				
	31053				
	31054	88	5.7	4.3 - 8.2	16
	31055				
	30156				
	31057				
	31074				
	31075				
	31019				
	31058				
	31059	59	5.9	4.7 - 7.6	2
	31060				
	31061				
	31064				
	31065				

Location	Station Number	No. of Samples	Mean* pH	Range	No. of Samples < pH 5.6
Toronto	31021	9	4.3	3.4 - 7.0	2
	31063	8	5.1	4.4 - 6.1	3
	31069	9	5.7	5.0 - 7.1	2
	31070	9	6.2	5.5 - 7.6	1
	31071	8	6.3	5.5 - 7.5	1
	31073	8	5.0	4.1 - 7.2	2
	31076	9	5.8	5.1 - 7.3	2
	31077	10	4.9	4.0 - 7.0	4
	31082	10	6.3	5.7 - 7.2	0
	31084	9	4.5	3.6 - 7.0	2
	31092	11	6.4	5.9 - 7.2	0
	31094	7	4.5	3.8 - 7.0	2
	31095	7	4.5	3.7 - 7.0	3
	31096	8	4.8	3.9 - 7.1	1
	31097	8	5.0	4.1 - 7.2	2
Scarbo-rough	33003	9	4.6	3.8 - 7.0	5
	33004	9	4.4	3.5 - 6.5	2
	33005	7	4.5	3.9 - 6.4	6
	33007	7	5.1	4.6 - 8.3	4
	33008	8	5.9	5.5 - 7.7	1
	33013	9	4.6	4.0 - 6.3	6
	33016	8	6.3	5.8 - 7.7	0
	33017	7	5.6	4.9 - 7.2	1
	33018	8	5.5	4.6 - 7.2	1
	33019	8	6.2	5.7 - 7.5	1
	33021	7	4.0	3.3 - 6.5	5
	33023	8	4.7	3.8 - 7.1	3

Location	Station Number	No. of Samples	Mean* pH	Range	No. of Samples < pH 5.6
Scarbo- rough	33024	7	3.8	3.0 - 6.6	4
	33025	4	4.6	4.3 - 5.8	3
	33029	8	5.1	4.3 - 7.0	2
North York	34001	7	5.1	4.6 - 7.3	3
	34002	7	4.0	3.3 - 6.5	4
	34006	6	5.8	5.4 - 6.6	2
	34007	8	4.5	3.8 - 6.3	5
	34008	7	5.6	5.1 - 6.6	2
	34013	8	4.6	4.1 - 6.0	5
	34016	9	5.7	5.1 - 7.5	2
Etobicoke	35002	7	6.0	5.3 - 6.8	0
	35003	8	4.5	3.8 - 7.4	4
	35005	7	5.0	4.3 - 6.3	3
	35009	8	4.2	3.6 - 6.4	4
	35010	9	6.0	5.6 - 6.9	0
	35011	8	5.9	5.4 - 6.6	1
	35012	8	5.3	4.6 - 6.8	3
	35014	10	4.4	3.7 - 6.6	4
	35015	8	4.7	4.3 - 5.8	7
	35017	10	5.6	5.0 - 6.9	3
	35018	10	5.9	5.3 - 7.1	2
	35019	7	6.3	6.0 - 7.0	0
	35033	8	4.6	3.7 - 6.5	4
	35036	6	5.8	5.3 - 7.2	1
	35037	9	6.1	5.7 - 6.8	0
	35039	7	4.3	3.5 - 6.5	2
	35040	6	5.14	4.5 - 6.8	2
	35041	7	4.5	3.7 - 7.0	3

Location	Station Number	No. of Samples	Mean* pH	Range	No. of Samples < pH 5.6
York	36009	7	5.5	4.9 - 6.4	2
	36012	7	5.2	4.6 - 6.3	3
	36015	8	6.3	6.0 - 7.5	0
Oakville	44005	8	4.5	3.9 - 6.8	5
	44006	9	5.9	5.2 - 7.5	2
	44010	7	3.9	3.4 - 7.6	5
Oshawa	45014	10	5.4	4.9 - 7.6	4
	45015	10	4.3	3.5 - 7.5	4
	45016	8	4.9	4.1 - 8.2	4
	45017	9	4.2	3.3 - 8.1	3
	45018	10	5.8	5.1 - 7.7	3
	45019	10	5.2	4.4 - 7.8	3
	45021	8	4.0	3.2 - 7.5	3
	45022	9	5.6	4.7 - 7.6	1
	45030	8	4.2	3.4 - 7.0	6
	45031	9	3.9	3.4 - 6.6	8
	45032	7	4.1	3.3 - 8.4	5
	45034	9	4.2	3.3 - 7.6	5
	45035	8	5.5	4.9 - 7.2	3
Mississauga	46001	9	5.6	4.8 - 6.6	1
	46006	7	6.7	6.1 - 7.6	0
	46008	10	4.9	4.2 - 7.3	4
	46009	10	4.6	4.0 - 6.6	4
	46010	9	4.8	4.0 - 6.8	4
	46011	6	4.6	3.8 - 7.1	3
	46016	10	5.8	5.3 - 6.7	2
	46027	9	4.1	3.3 - 7.9	2
	46028	8	4.8	4.1 - 6.8	3
	46029	7	6.7	6.3 - 7.8	0
	46031	9	4.9	4.2 - 7.3	4

Location	Station Number	No. of Samples	Mean* pH	Range	No. of Samples < pH 5.6
Bramalea	46033	7	5.7	5.1 - 7.3	1
Mississauga	46041	6	5.3	4.8 - 6.1	4
	46042	10	5.3	4.4 - 7.5	3
	46044	10	4.5	3.8 - 7.3	2
	46045	9	4.9	4.2 - 6.9	6
	46046	8	5.2	4.8 - 5.9	7
Port Hope	58026	6	5.8	5.5 - 6.7	1
	58027	7	4.6	3.9 - 6.4	4
	58028	8	5.1	4.2 - 7.1	2
	58029	9	4.8	3.8 - 7.7	1
Peter borough	59003	5	4.9	4.6 - 7.3	3
	59004	7	4.6	4.2 - 6.4	5
	59006	6	4.3	3.5 - 7.6	1

* Calculated as the negative logarithm of arithmetic mean hydrogen ion concentration .

Table 5 Mean pH of Bulk Precipitation during August, 1977
in Urban Centers along Upper Lake Ontario

Location	No. of Stations	Min.pH	Max.pH	Avg.pH [*]
Barrie	1	3.6	3.6	3.6
Bomanville	2	4.5	5.5	4.8
Collingwood	3	3.7	8.0	4.2
Etobicoke	13	3.5	6.7	4.0
Markham	1	3.6	3.6	3.6
Mississauga	7	3.8	6.3	4.3
Newmarket	2	3.6	4.2	3.8
North York	6	3.8	6.6	4.2
Oakville	8	3.4	7.0	4.0
Oshawa	13	3.3	6.6	3.7
Peterborough	2	3.5	4.7	3.8
Port Hope	4	3.8	6.7	4.2
Richmond Hill	2	3.9	4.0	3.9
Scarborough	14	3.0	6.9	3.8
Toronto	49	3.4	7.2	4.2

* Calculated as the negative logarithm of arithmetic mean hydrogen ion concentration .

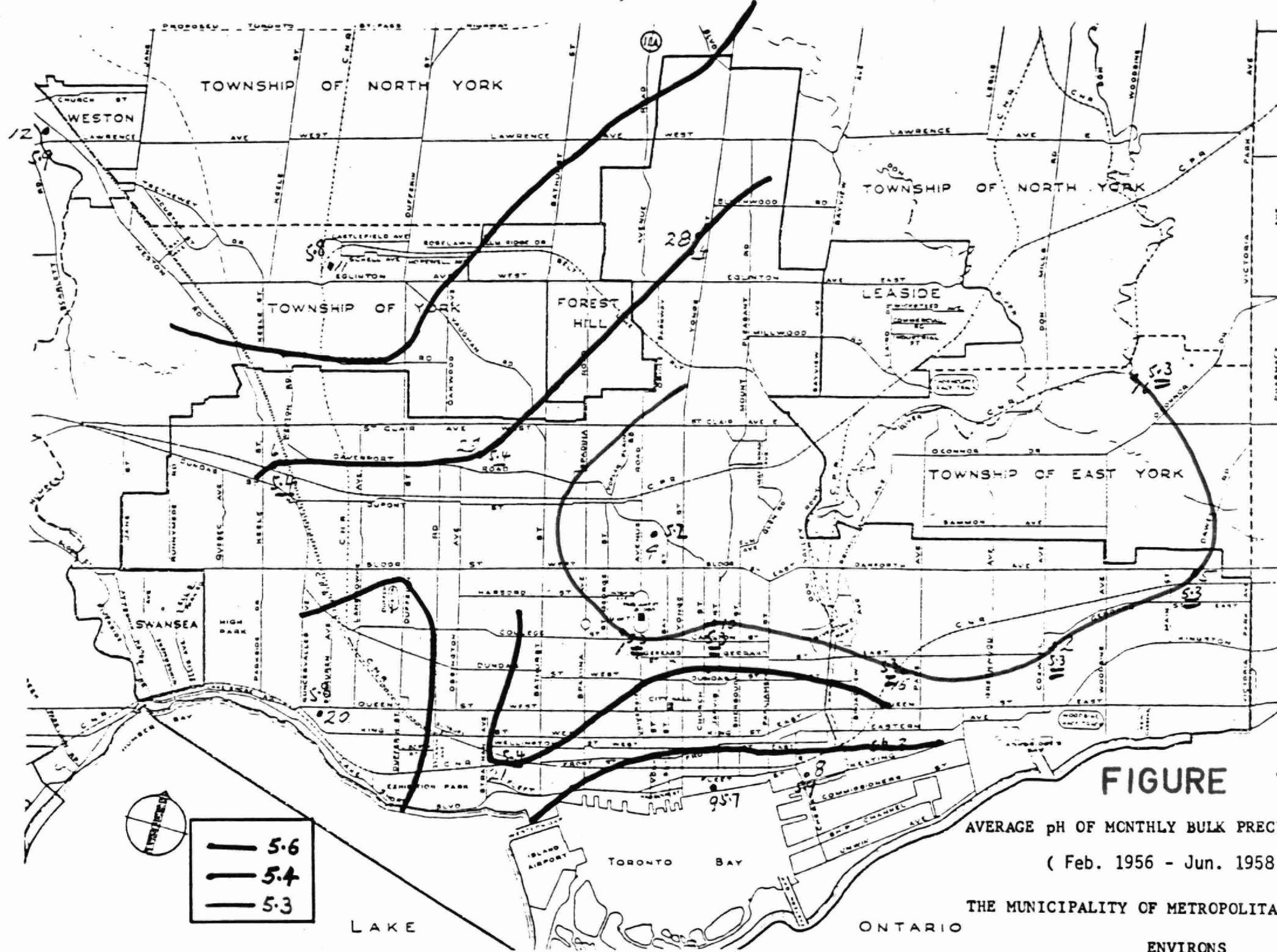
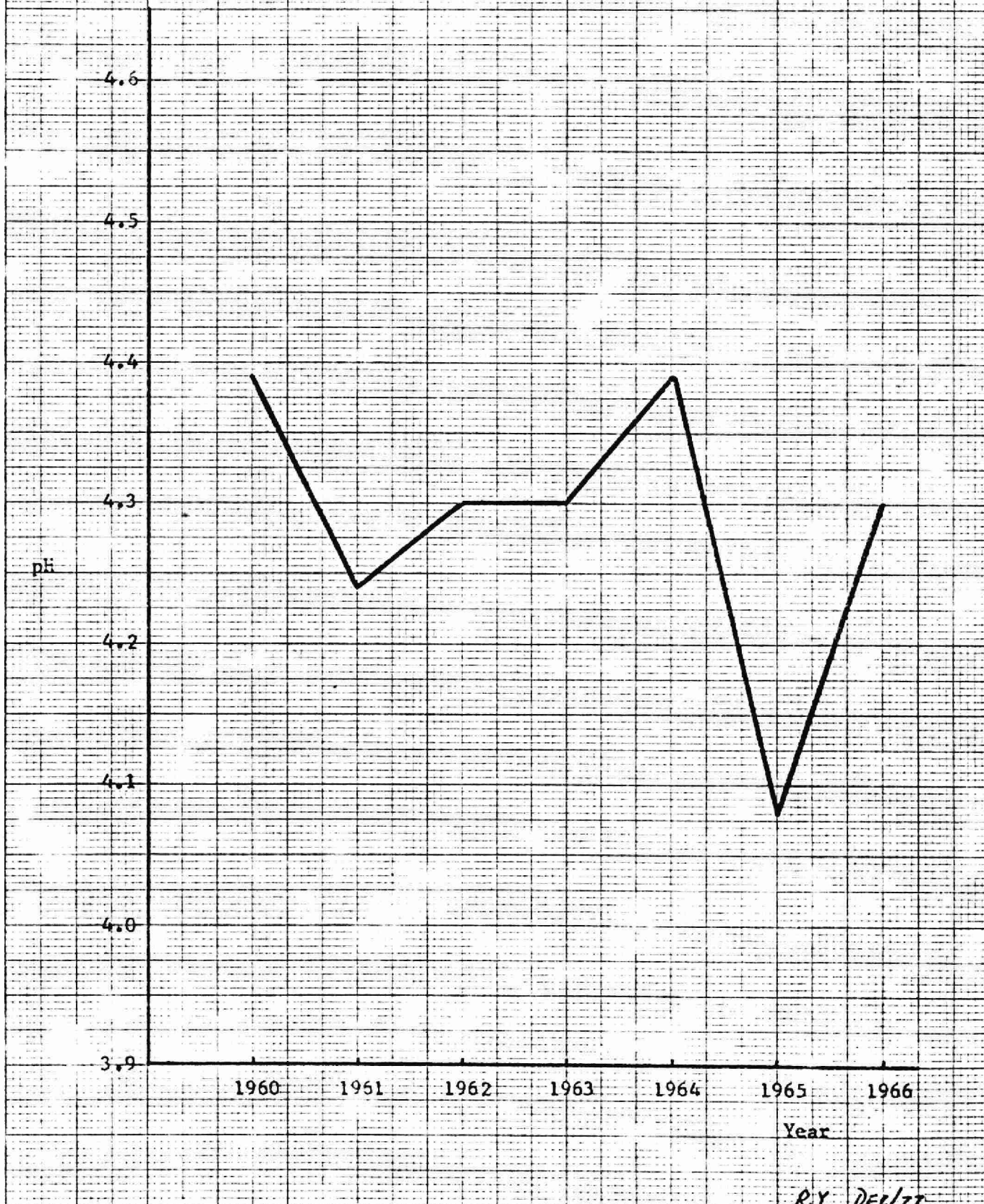


FIGURE 1

AVERAGE pH OF MONTHLY BULK PRECIPITATION SAMPLES
(Feb. 1956 - Jun. 1958) IN

THE MUNICIPALITY OF METROPOLITAN TORONTO AND
O
ENVIRONS

Figure 2
Annual pH Of Monthly Bulk Precipitation Samples At
67 College Street, Toronto



R.Y. DEC/77

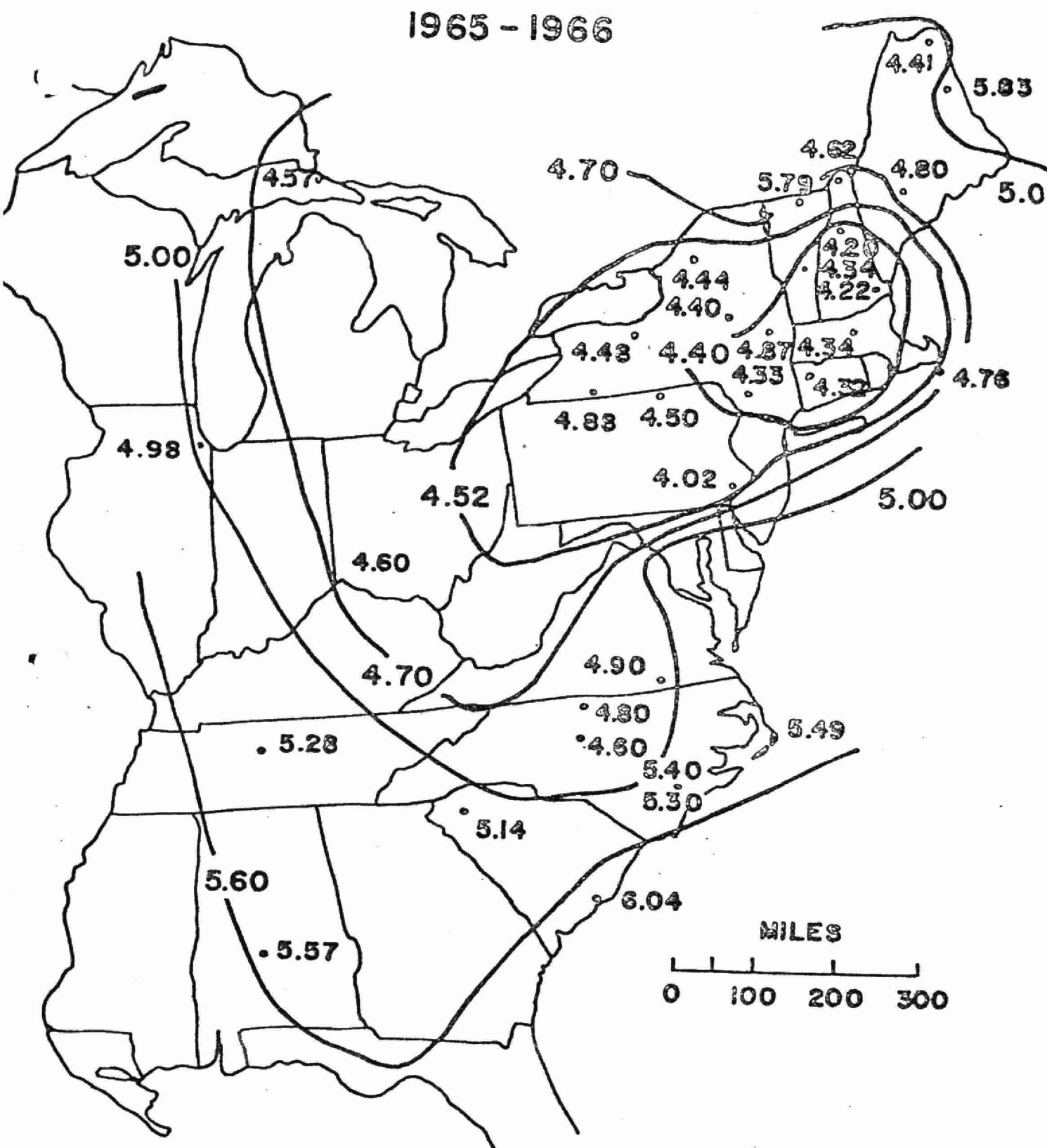


FIGURE 3
 PREDICTED PH OF PRECIPITATION OVER THE EASTERN UNITED STATES
 DURING THE PERIOD 1965-1966 BASED ON CHEMICAL DATA OF LODGE
 ET AL. 1968, GAMBELL AND FISHER 1966. FROM COGBILL AND
 LIKENS (1974).

1955 - 1956

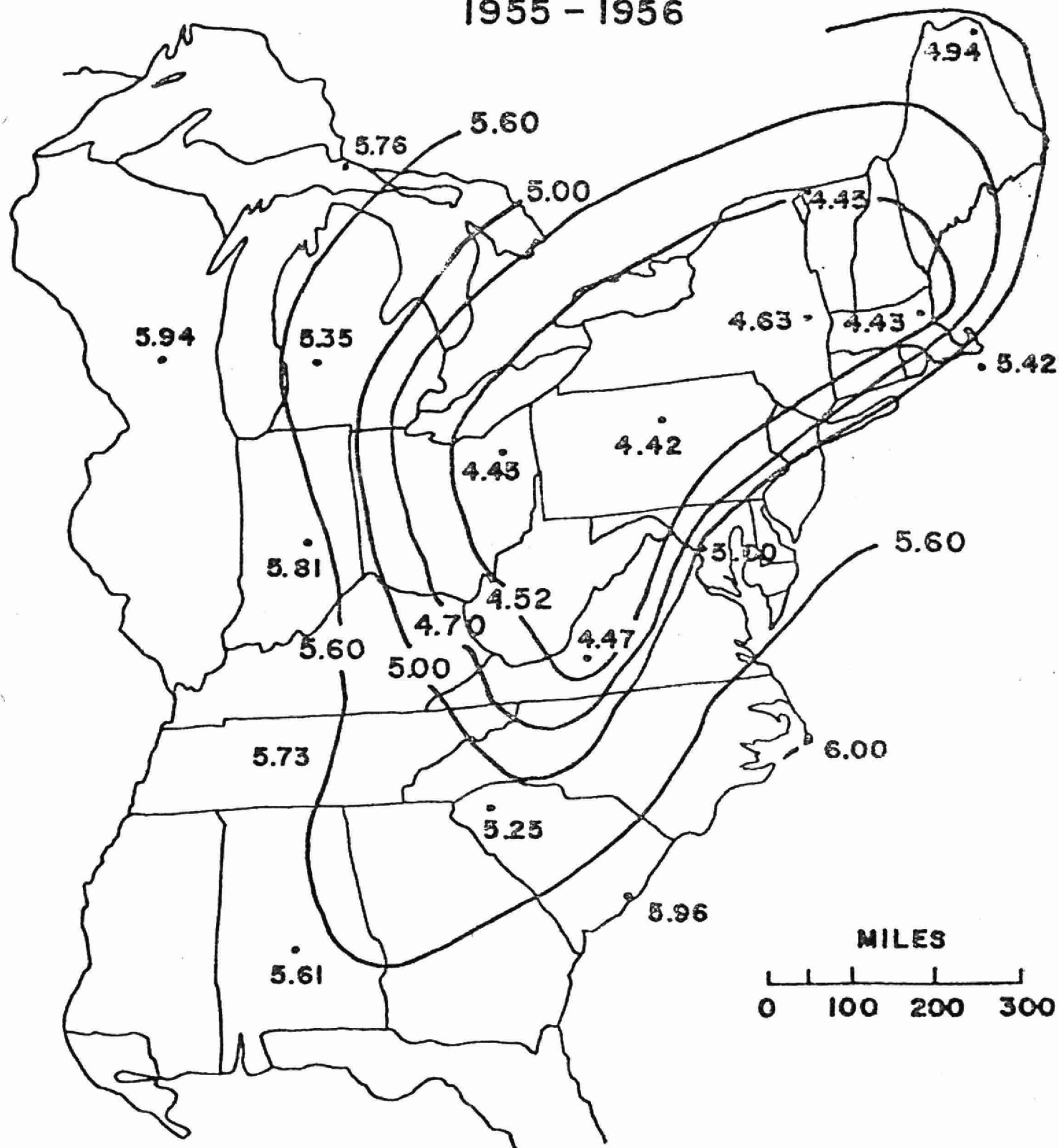


FIGURE 4
PREDICTED PH OF PRECIPITATION OVER THE EASTERN UNITED STATES
DURING THE PERIOD 1955-1956 BASED ON CHEMICAL DATA OF
JUNGE (1958) AND JUNGE AND WERBY (1958) FROM COGBILL
AND LIKENS (1974)

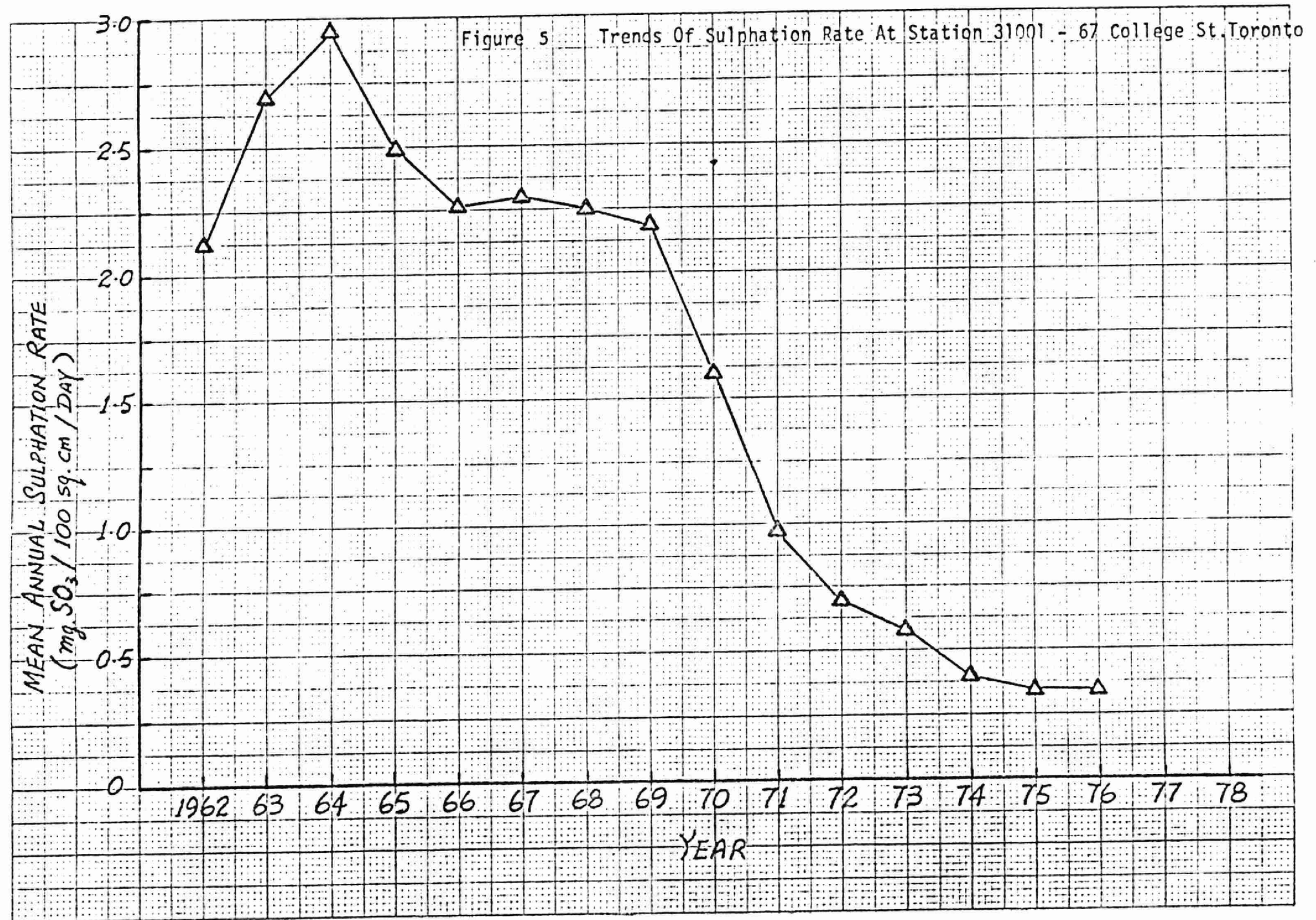


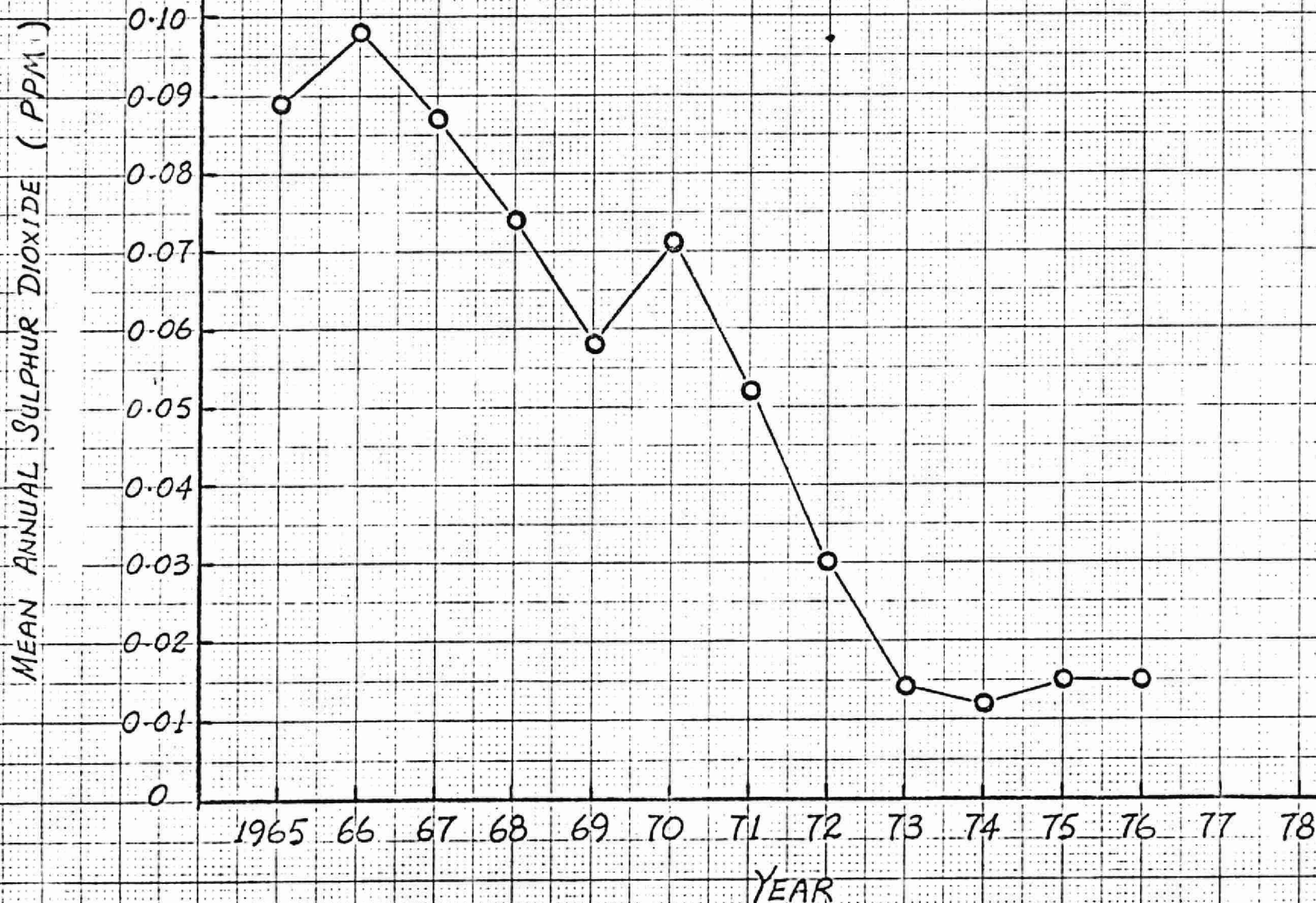
Figure 6 Trends Of Sulphur Dioxide At Station 31001 - 67 College St., Toronto

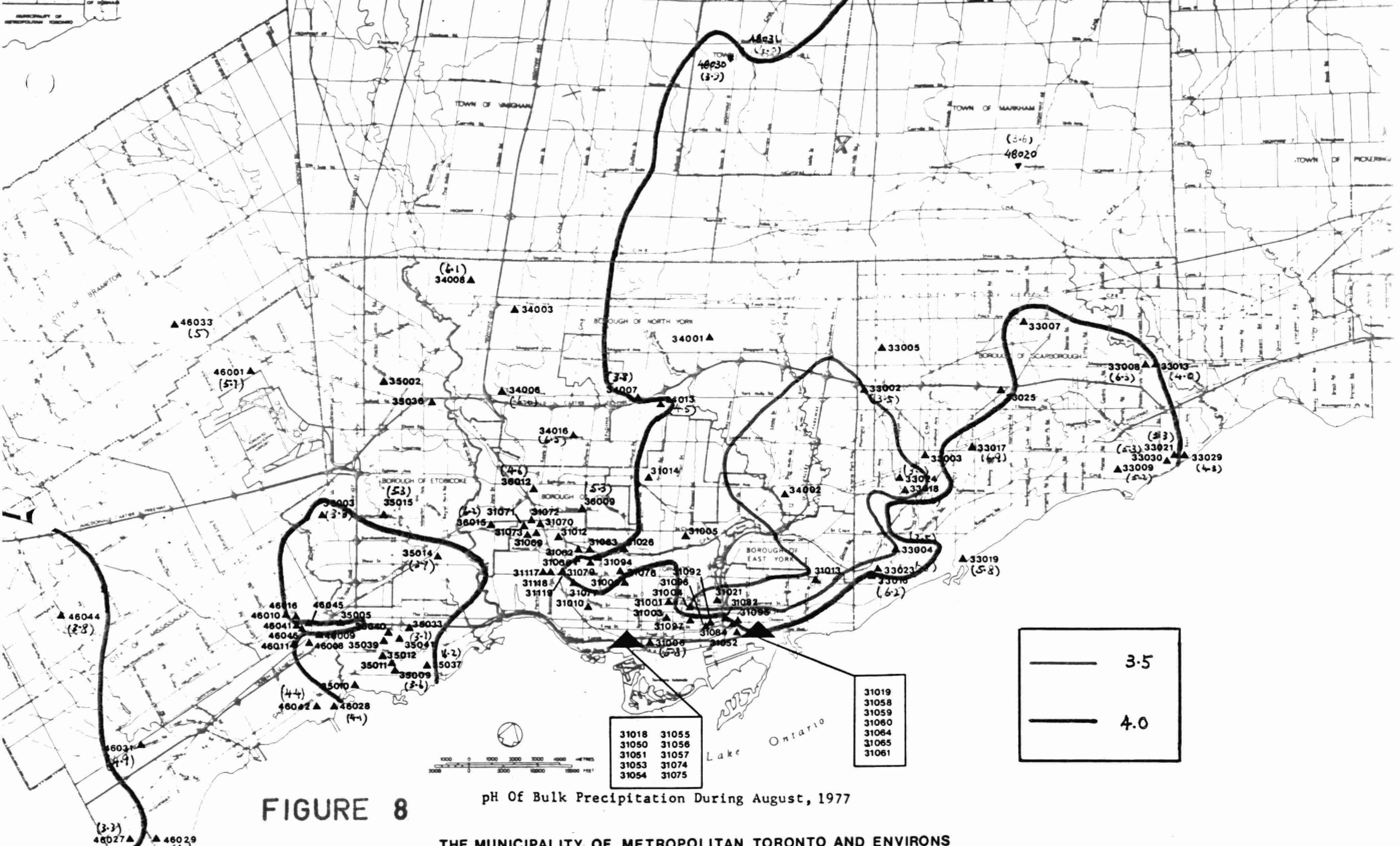
MEAN ANNUAL SULPHUR DIOXIDE (PPM)

0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0

1965 66 67 68 69 70 71 72 73 74 75 76 77 78

YEAR





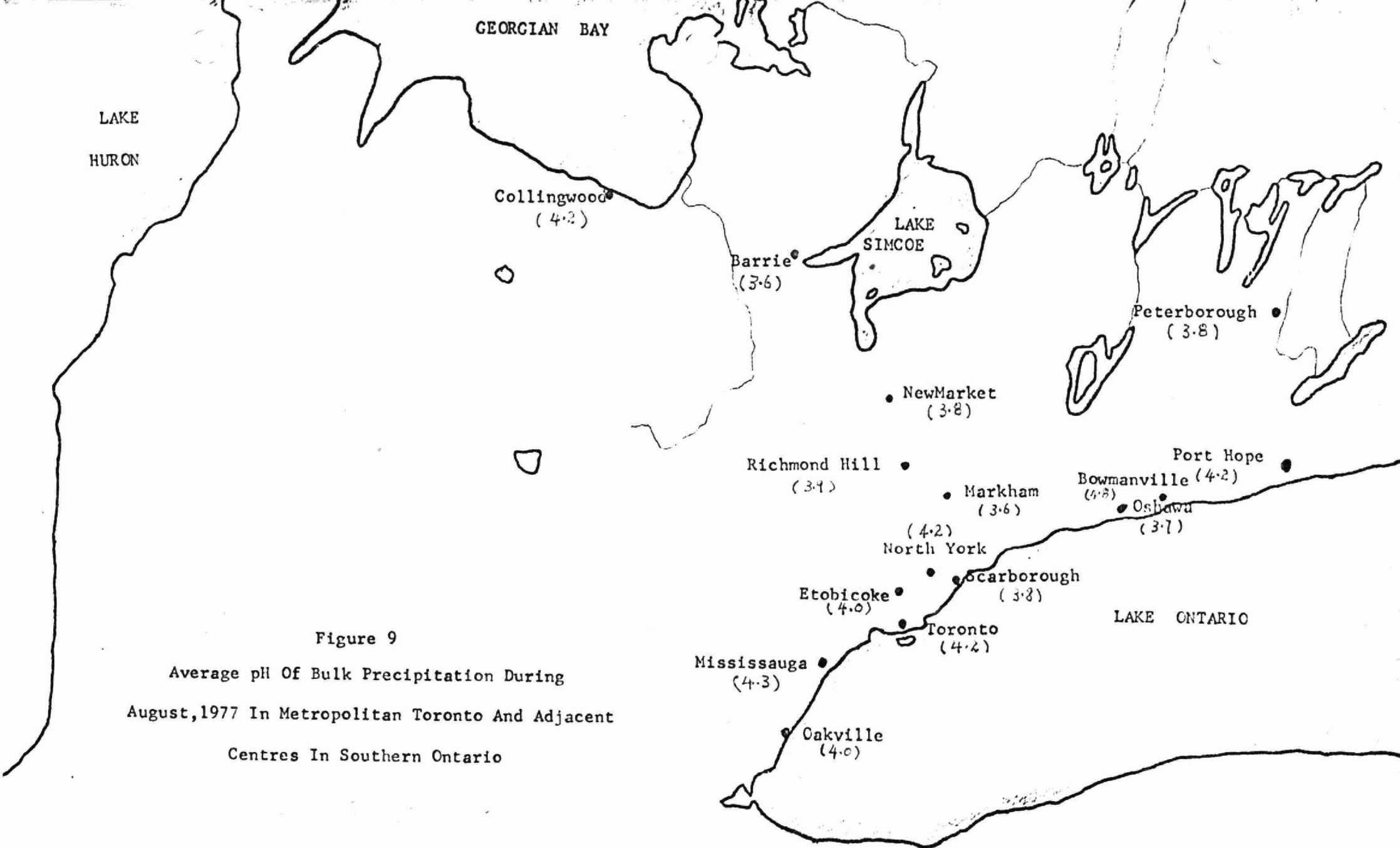
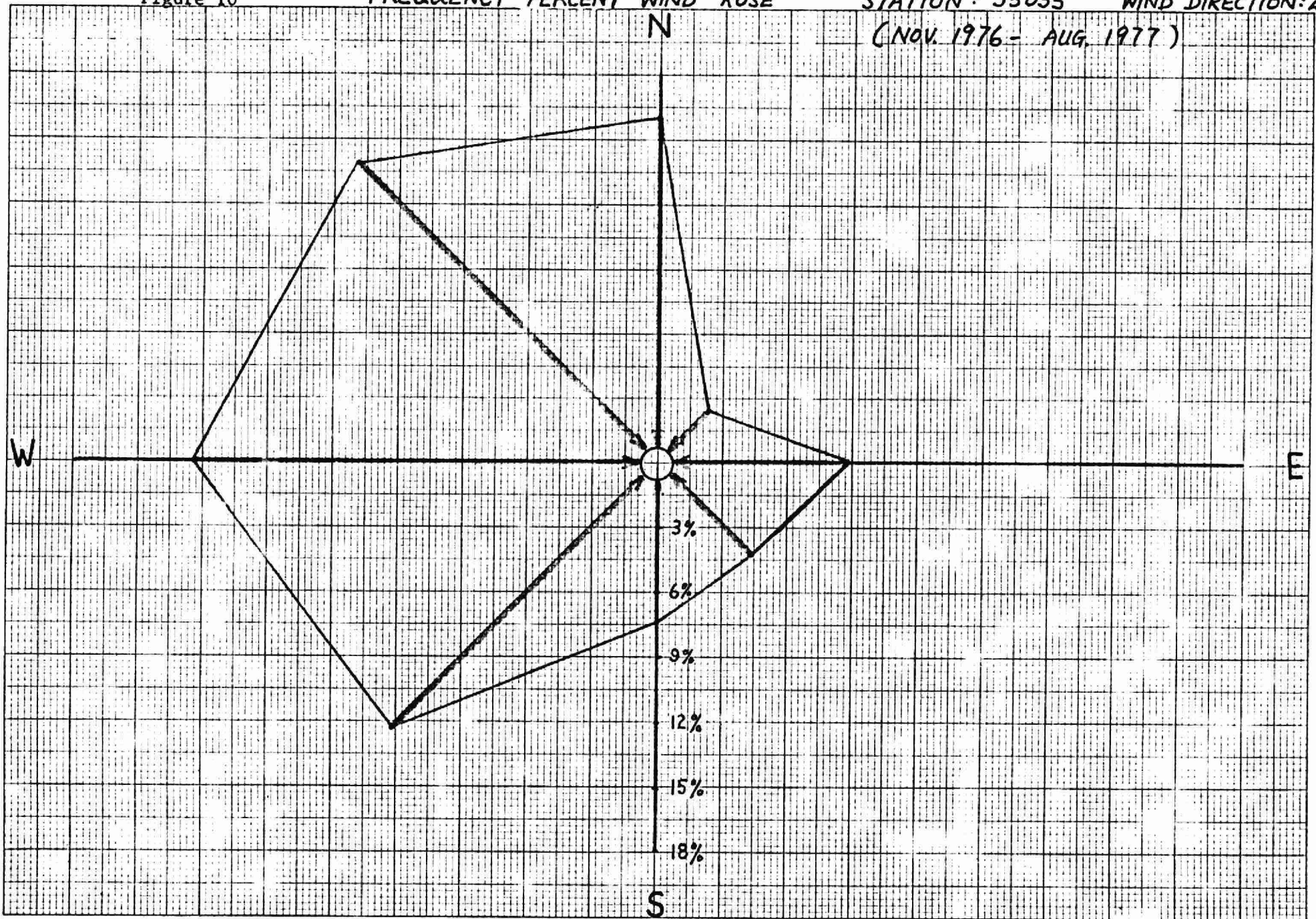


Figure 9
Average pH Of Bulk Precipitation During
August, 1977 In Metropolitan Toronto And Adjacent
Centres In Southern Ontario

Figure 10

FREQUENCY PERCENT WIND ROSE

STATION : 35033 WIND DIRECTION: 2
(NOV. 1976 - AUG. 1977)

R.Y. Nov/77

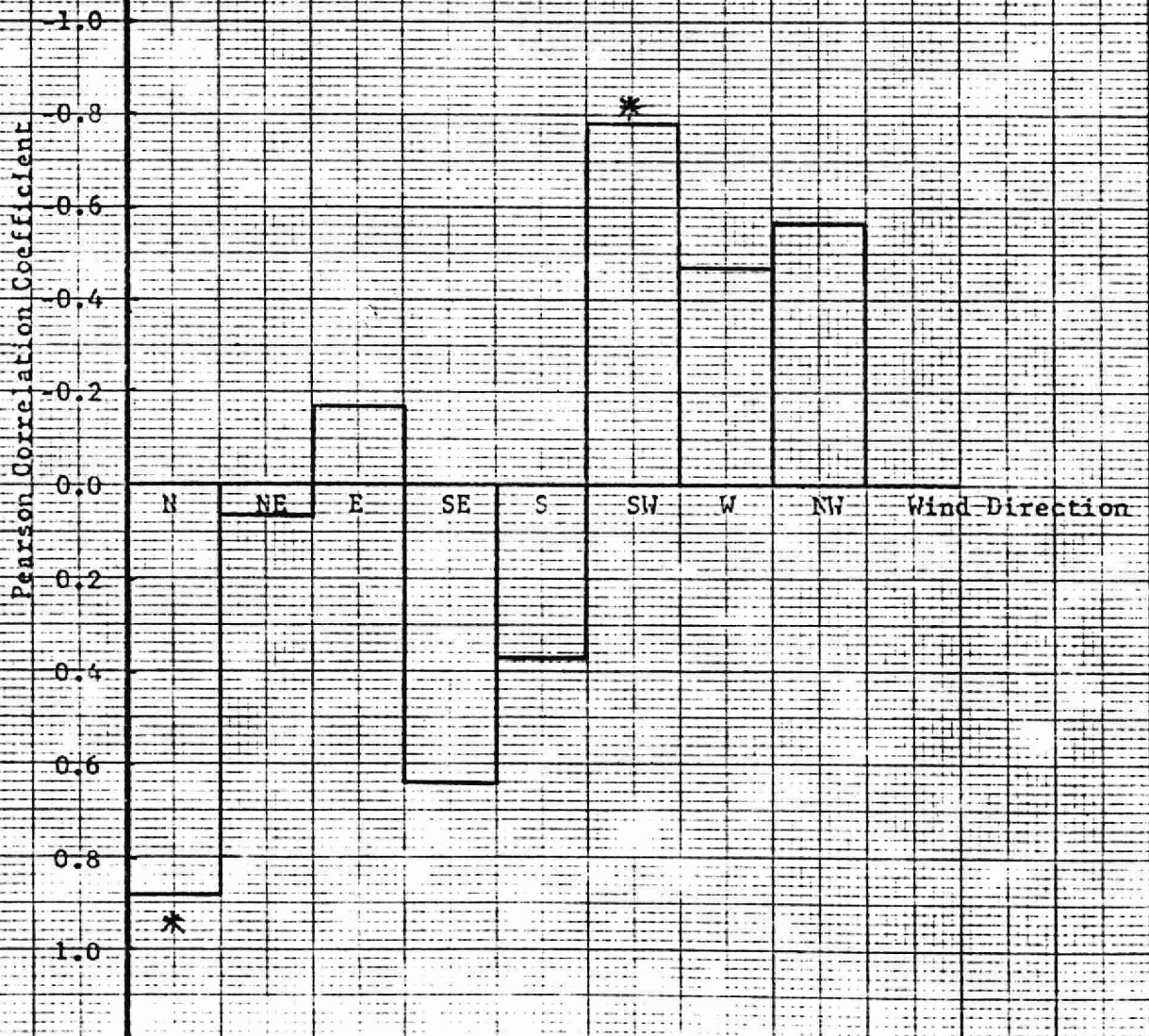
Figure 11

Pearson Correlation Coefficient of

Monthly pH's of Bulk Precipitation Samples With Logarithm of Hours of Wind

Station: 44010
(Oakville)

n = 7



* - Significant Wind Direction

Figure 12

Pearson Correlation Coefficient of

Monthly pht's of Bulk Precipitation Samples With Logarithm of Hours of Wind

Station: 46010
(Mississauga)

n = 9

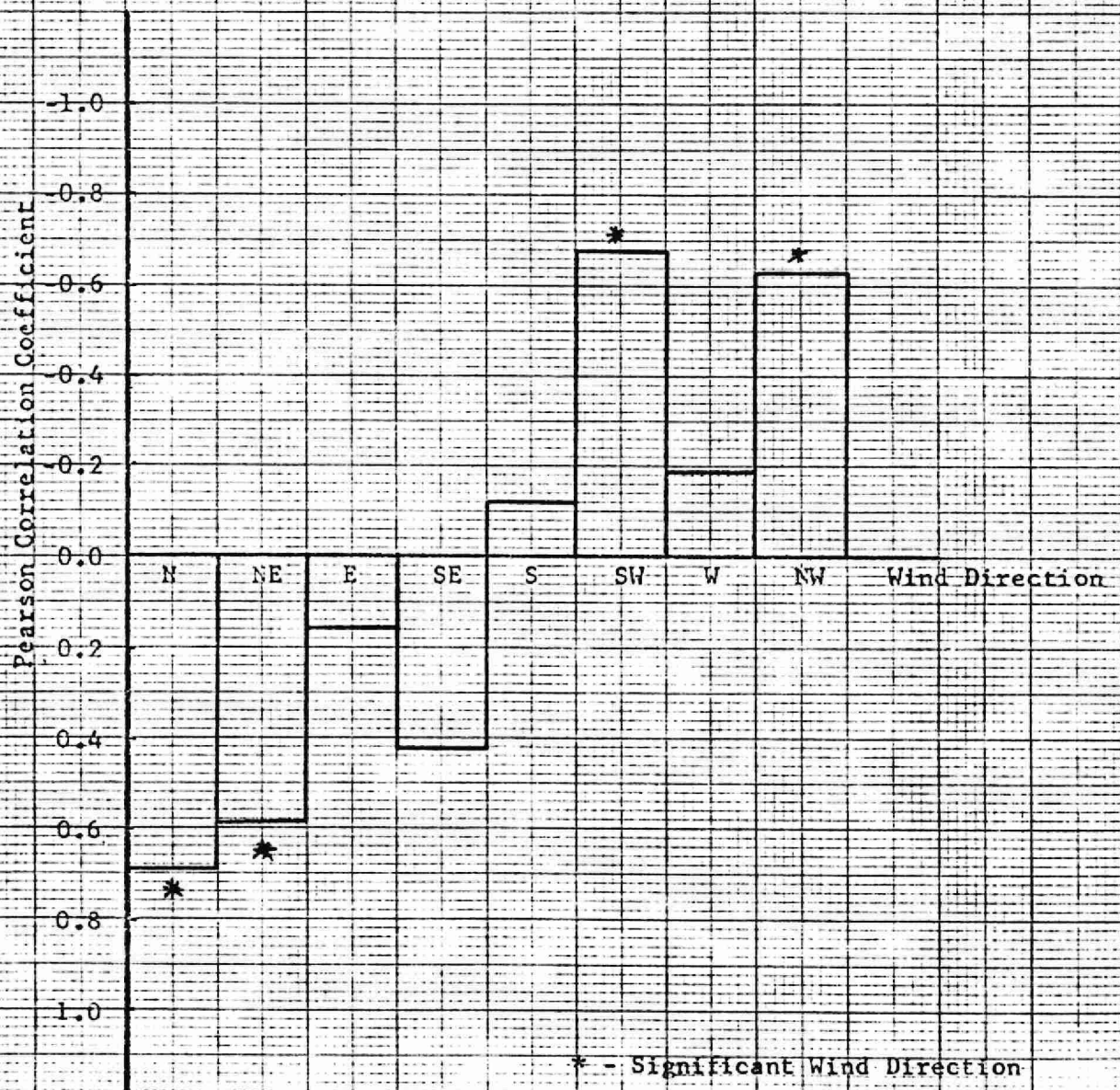
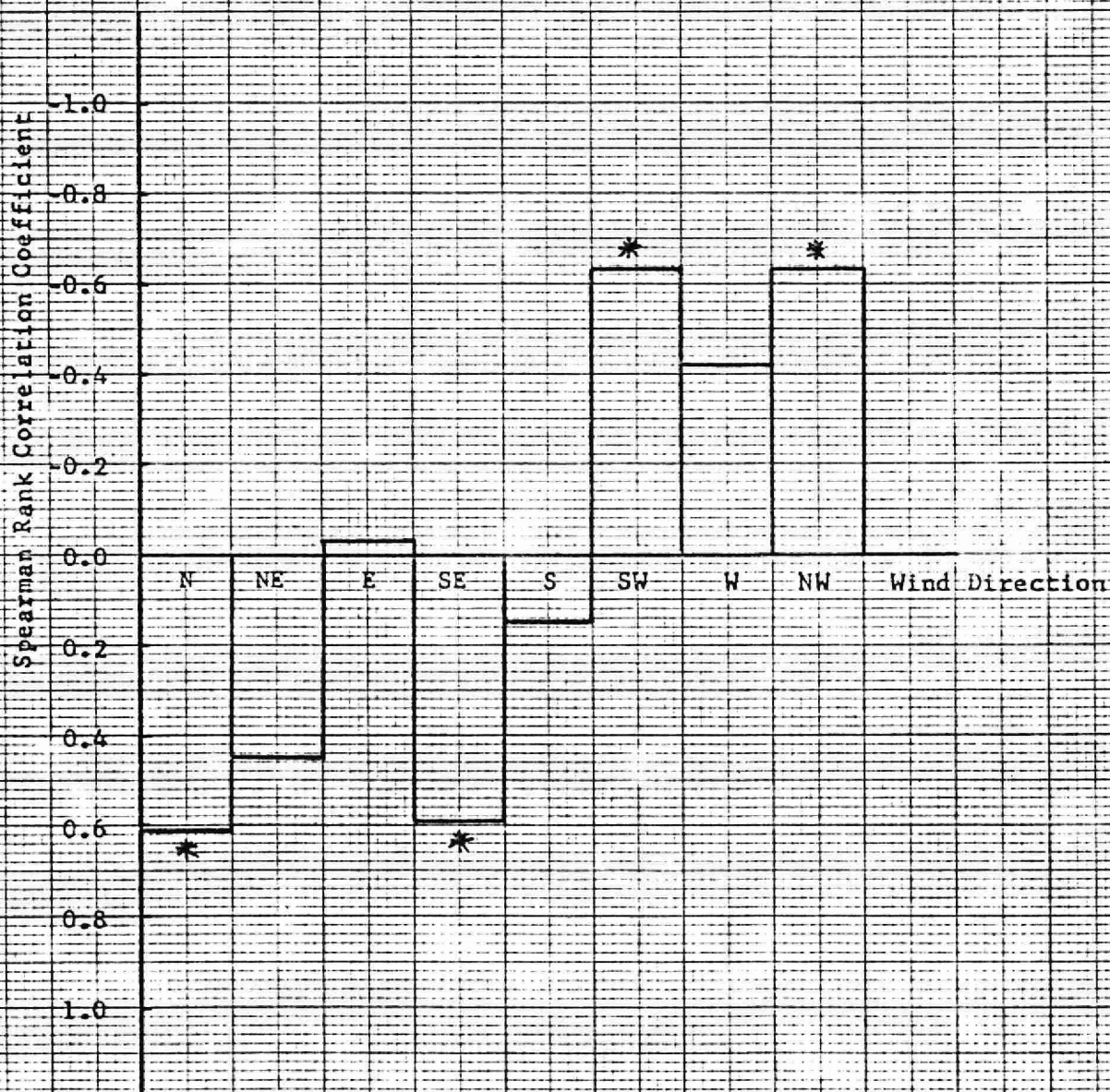


Figure 13

Spearman Rank Correlation Of Monthly pH's Of
Bulk-Precipitation Samples With Hours Of Wind

Station: 46031
(Mississauga)

$n =$ 9



* - Significant Wind Direction

Figure 14

Pearson Correlation Coefficient of

Monthly pH's of Bulk Precipitation Samples With Logarithm of Hours of Wind

Station: 35014

n = 10

(Etobicoke)

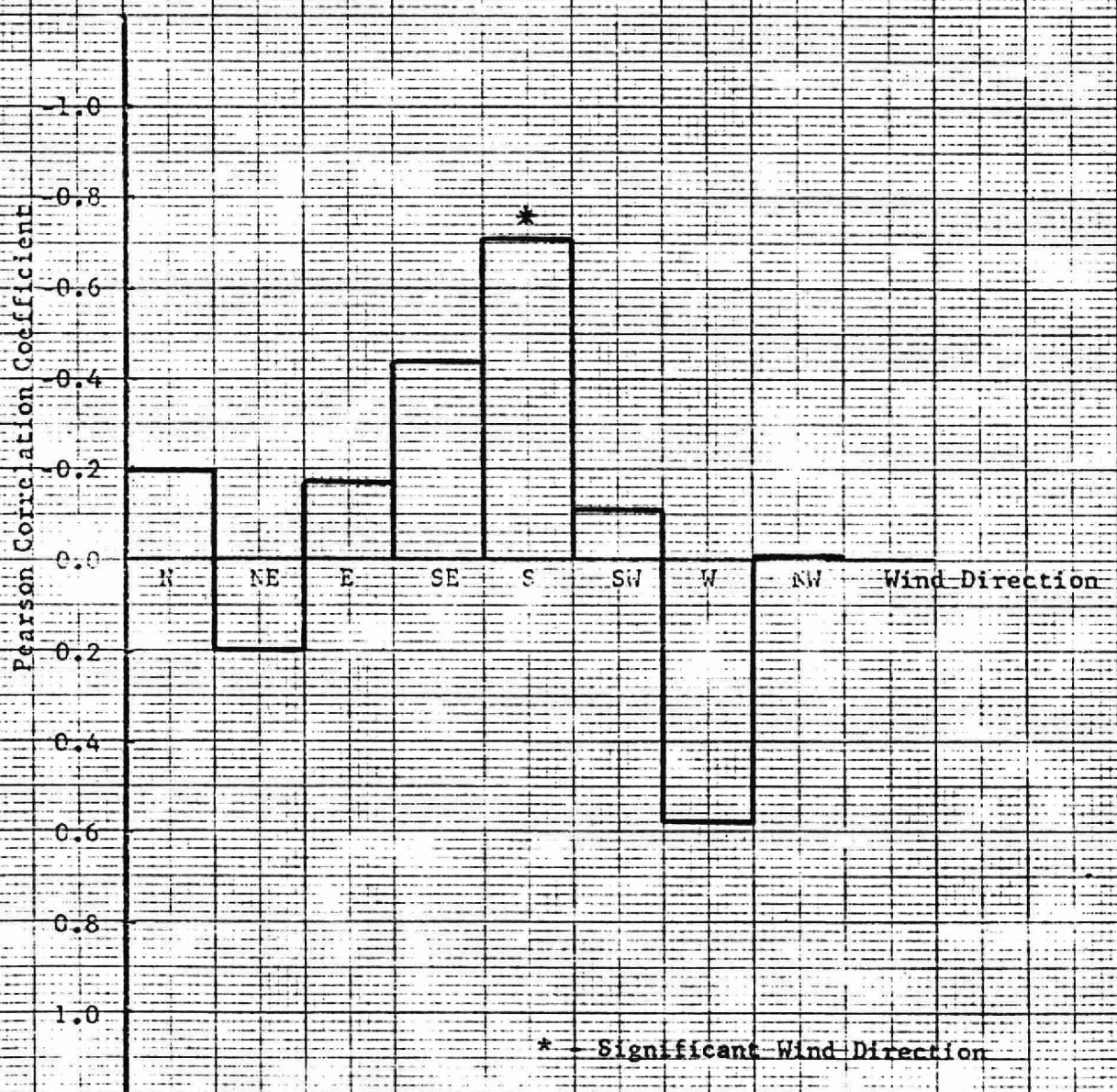


Figure 15

Pearson Correlation Coefficient of

Monthly pH's of Bulk Precipitation Samples With Logarithm of Hours of Wind

Station: 34001

n = 7

(North York)

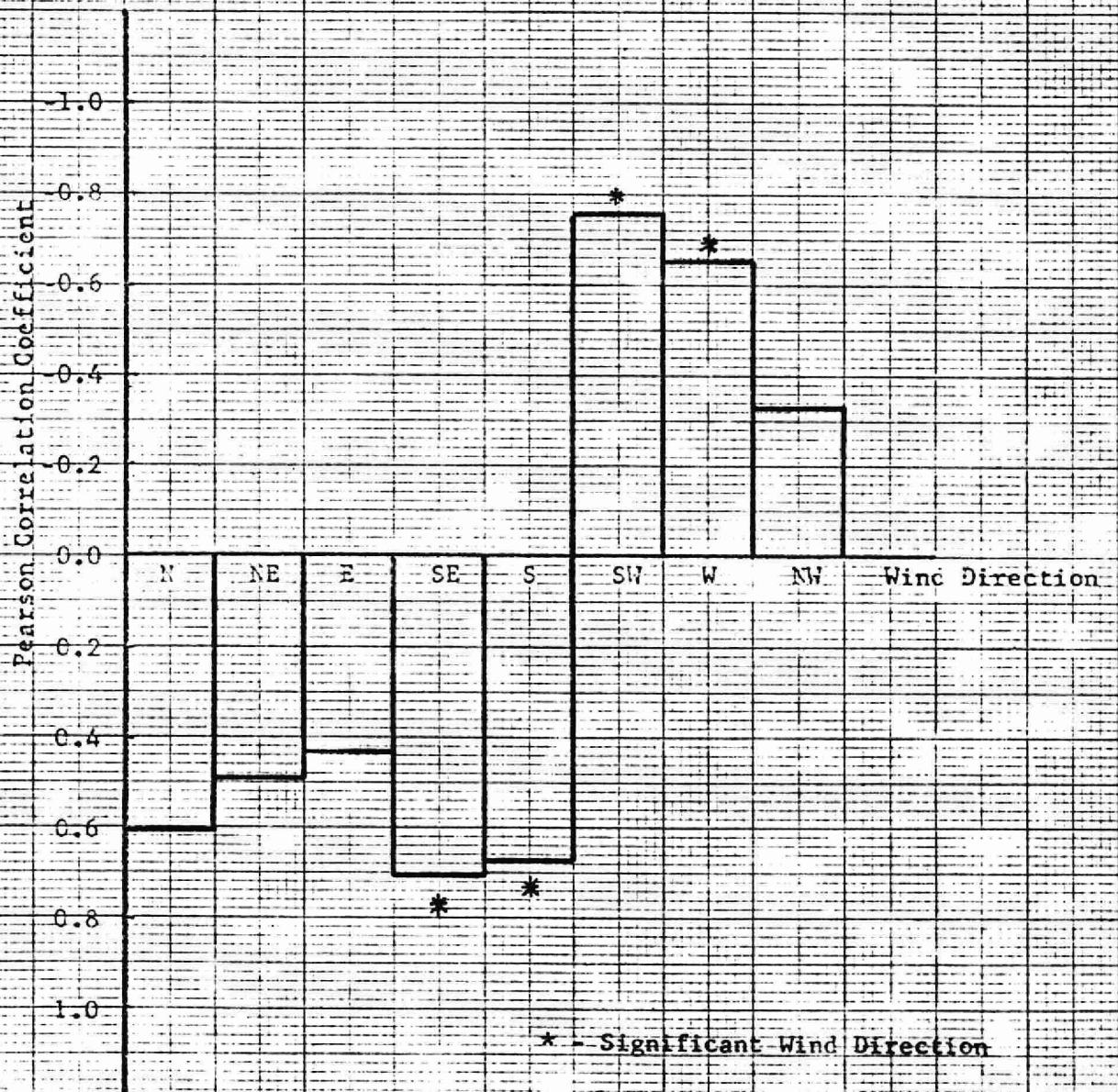
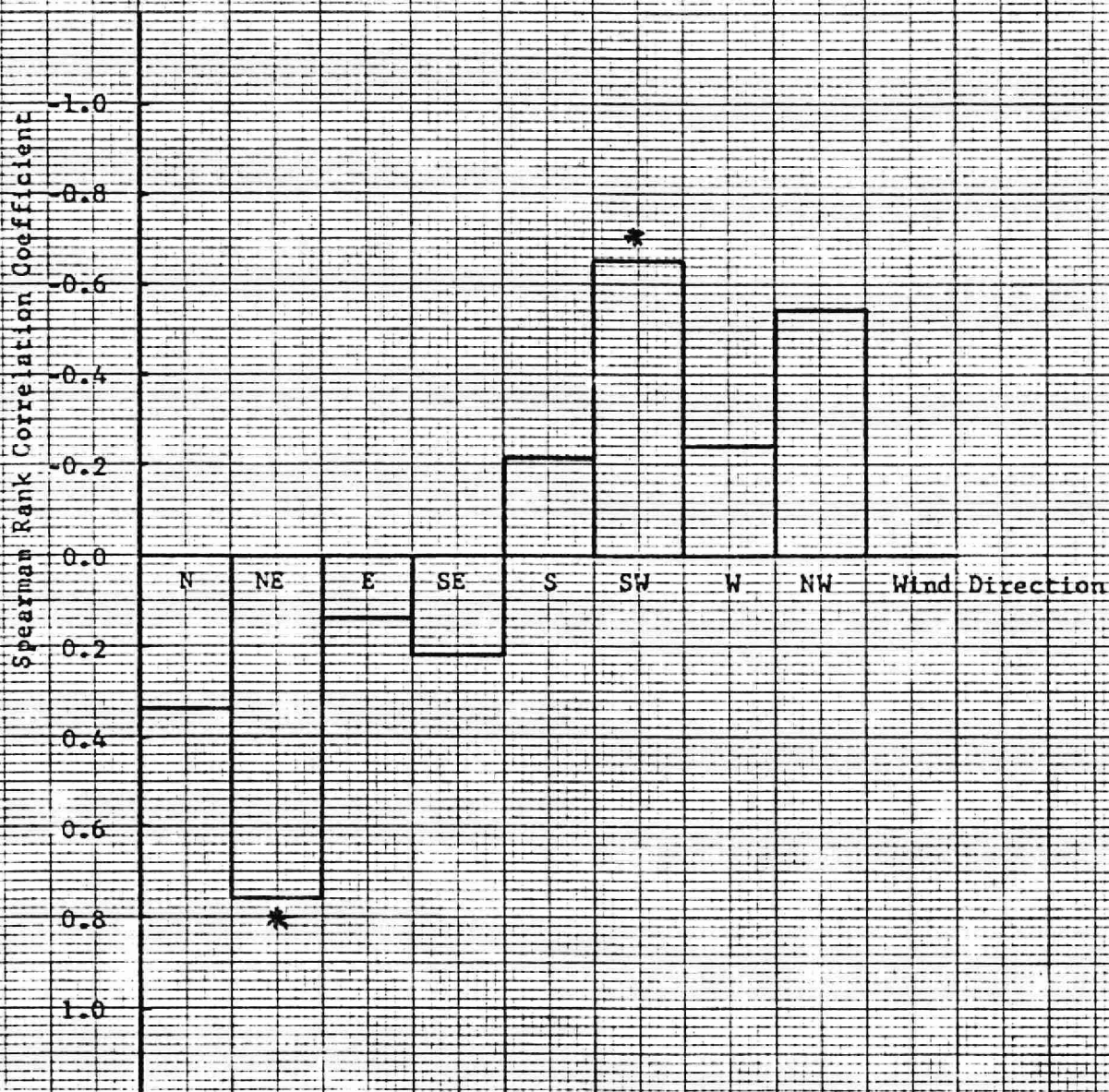


Figure 16

Spearman Rank Correlation Of Monthly pH's Of
Bulk Precipitation Samples With Hours Of Wind

Station: 34007
(North York)

n = 8



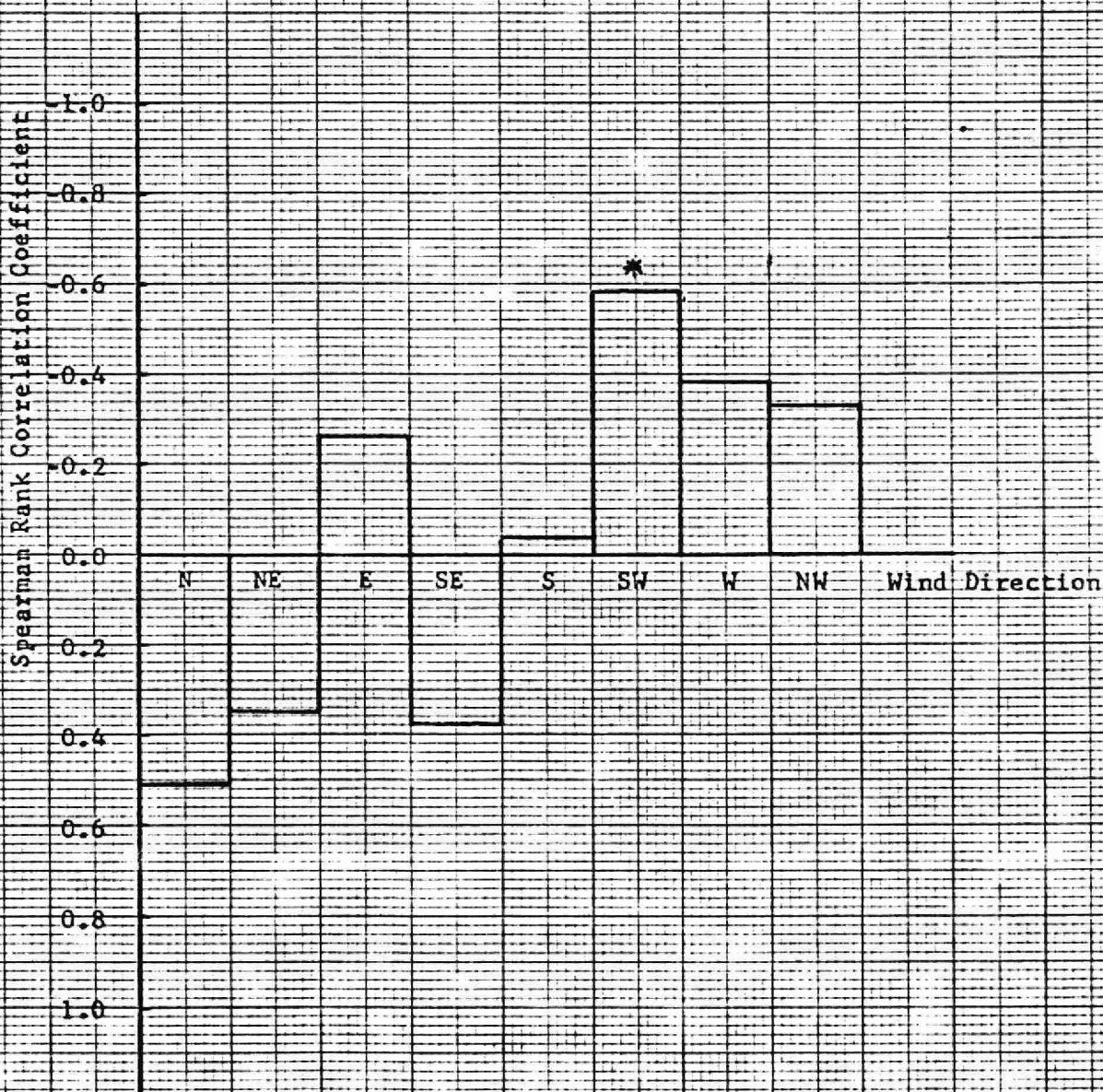
* - Significant Wind Direction

Figure 17

Spearman Rank Correlation Of Monthly pH's Of
Bulk-Precipitation Samples With Hours Of Wind

Station: 31005
 (Toronto)

n = 10



* - Significant Wind Direction

Figure 18

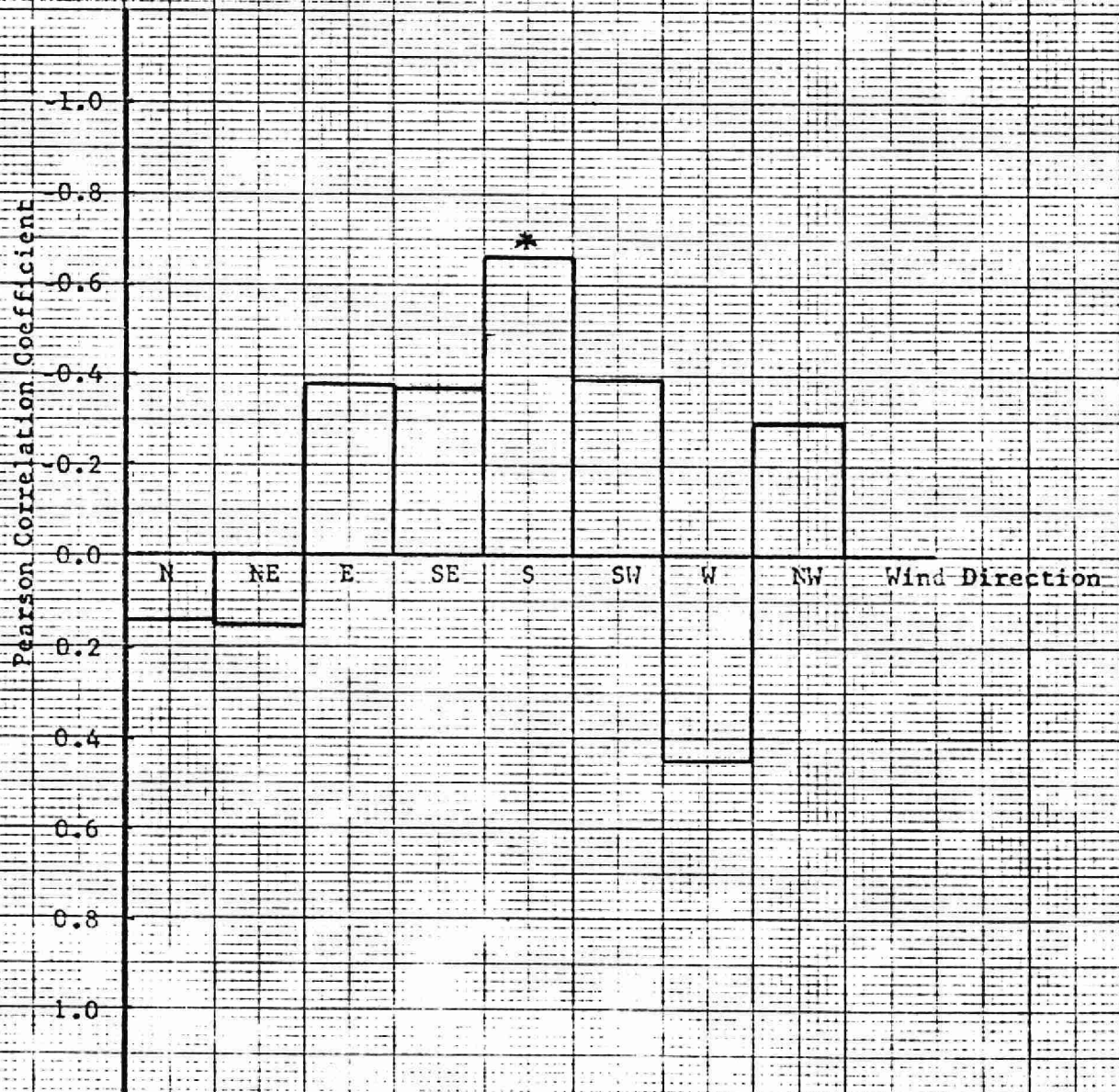
Pearson Correlation Coefficient of

Monthly pH's of Bulk Precipitation Samples With Logarithm of Hours of Wind

Station: 31914

n = 8

(Toronto)



* - Significant Wind Direction

Figure 19

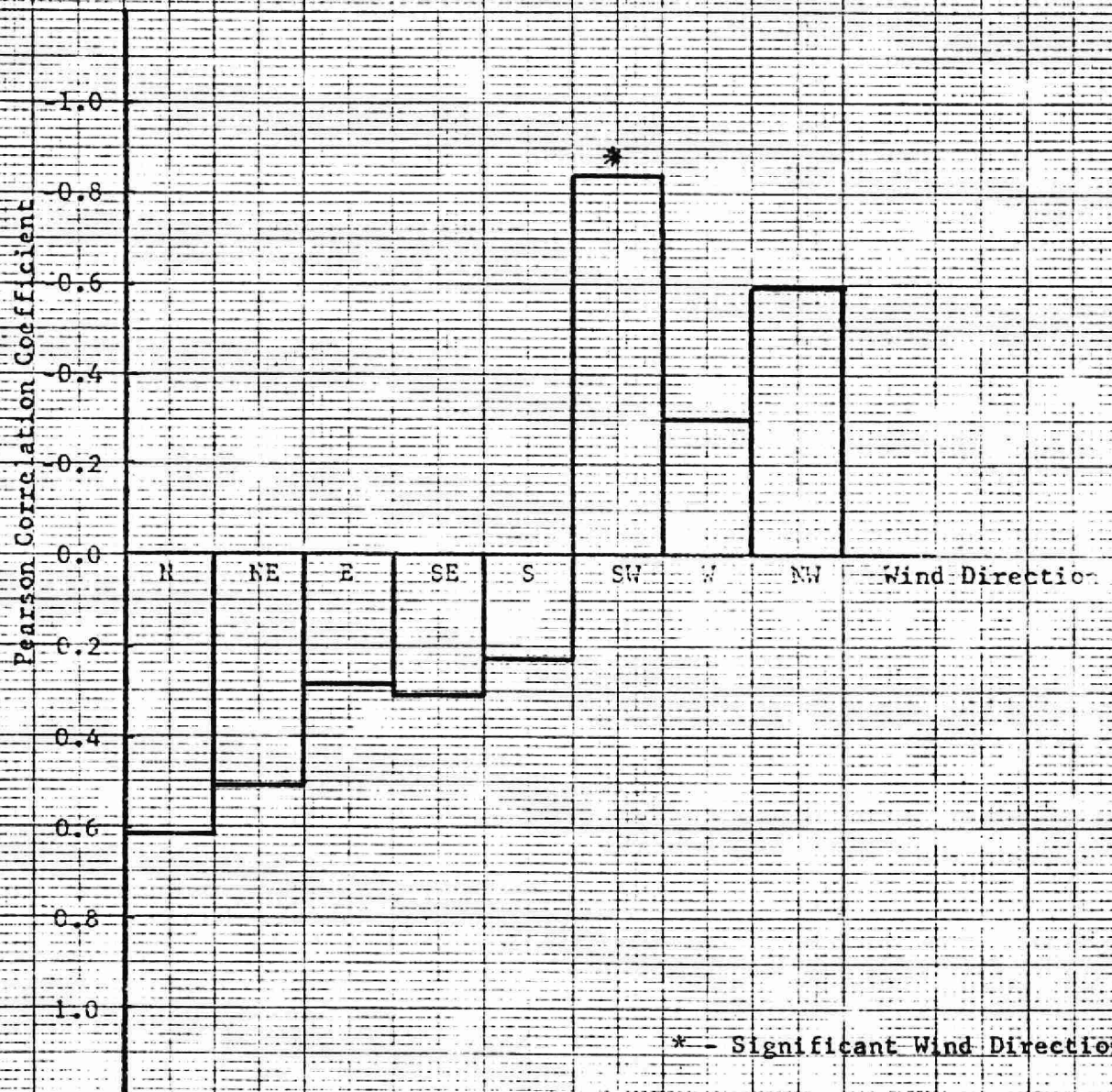
Pearson Correlation Coefficient of

Monthly pH's of Bulk Precipitation Samples With Logarithm of Hours of Wind

Station: 33024

n = 7

(Scarborough)



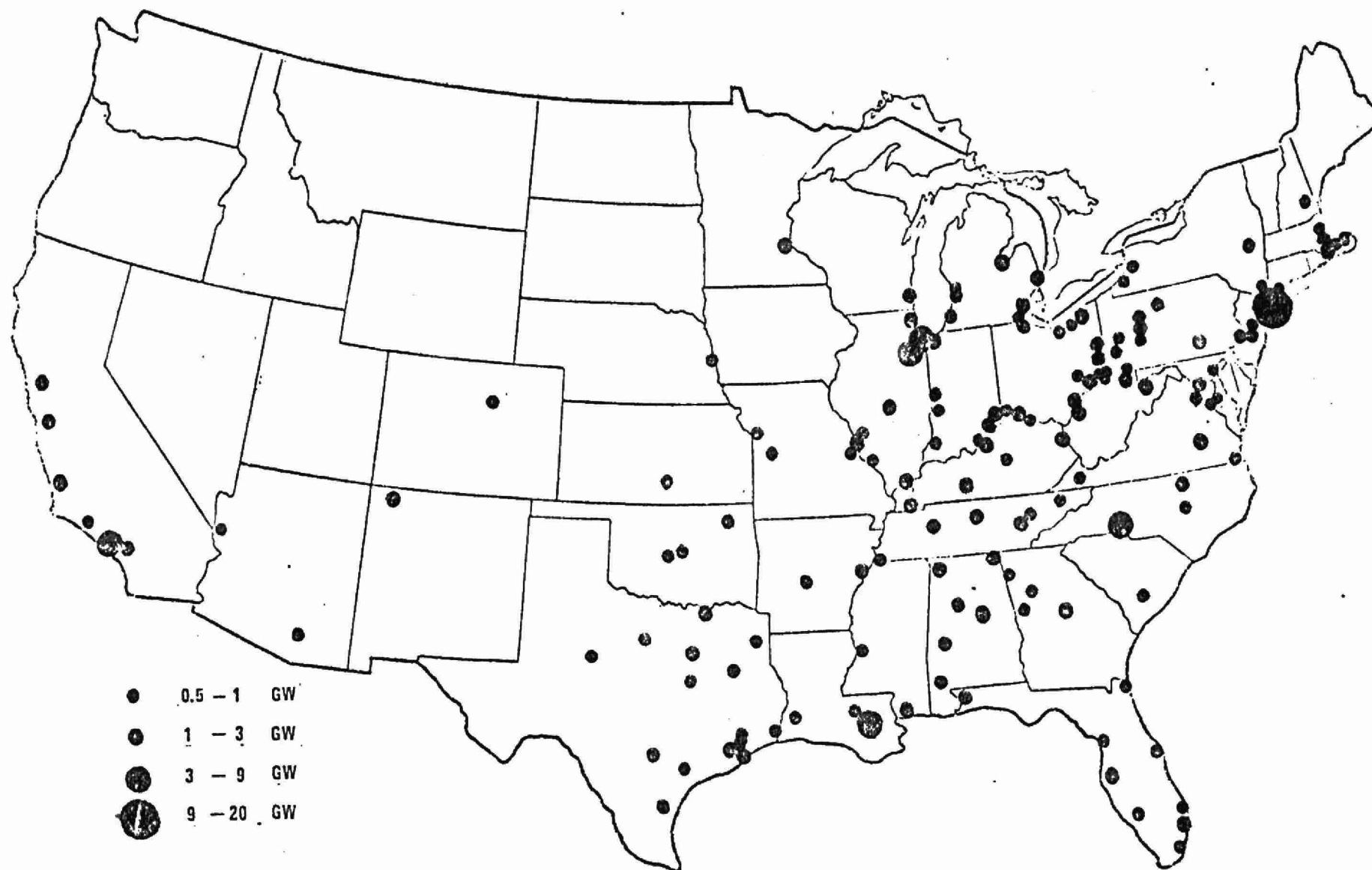


Figure 20 Fossil steam generating capacity, 1970.²⁶

Reproduced from EPA Report, "Position Paper On
Regulation Of Atmospheric Sulfates".

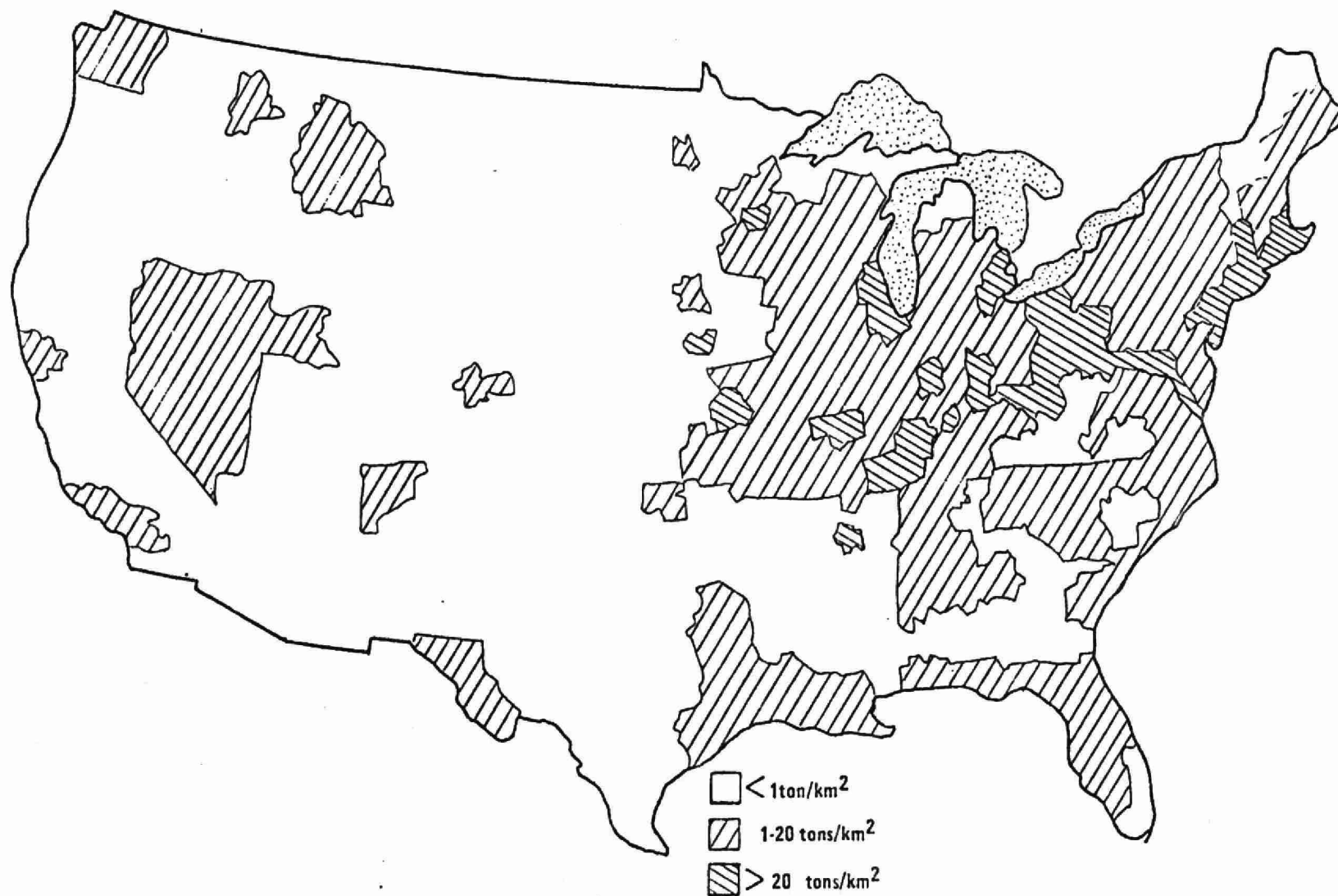


Figure 21 Nationwide geographic variation in annual SO_2 emission density.²⁷

Reproduced from EPA Report, "Position Paper On Regulation Of Atmospheric Sulfates".

Figure 22

Variations Of Ambient pH Of Bulk Precipitation Samples And Acid Fallout
At Station 31014, Toronto.

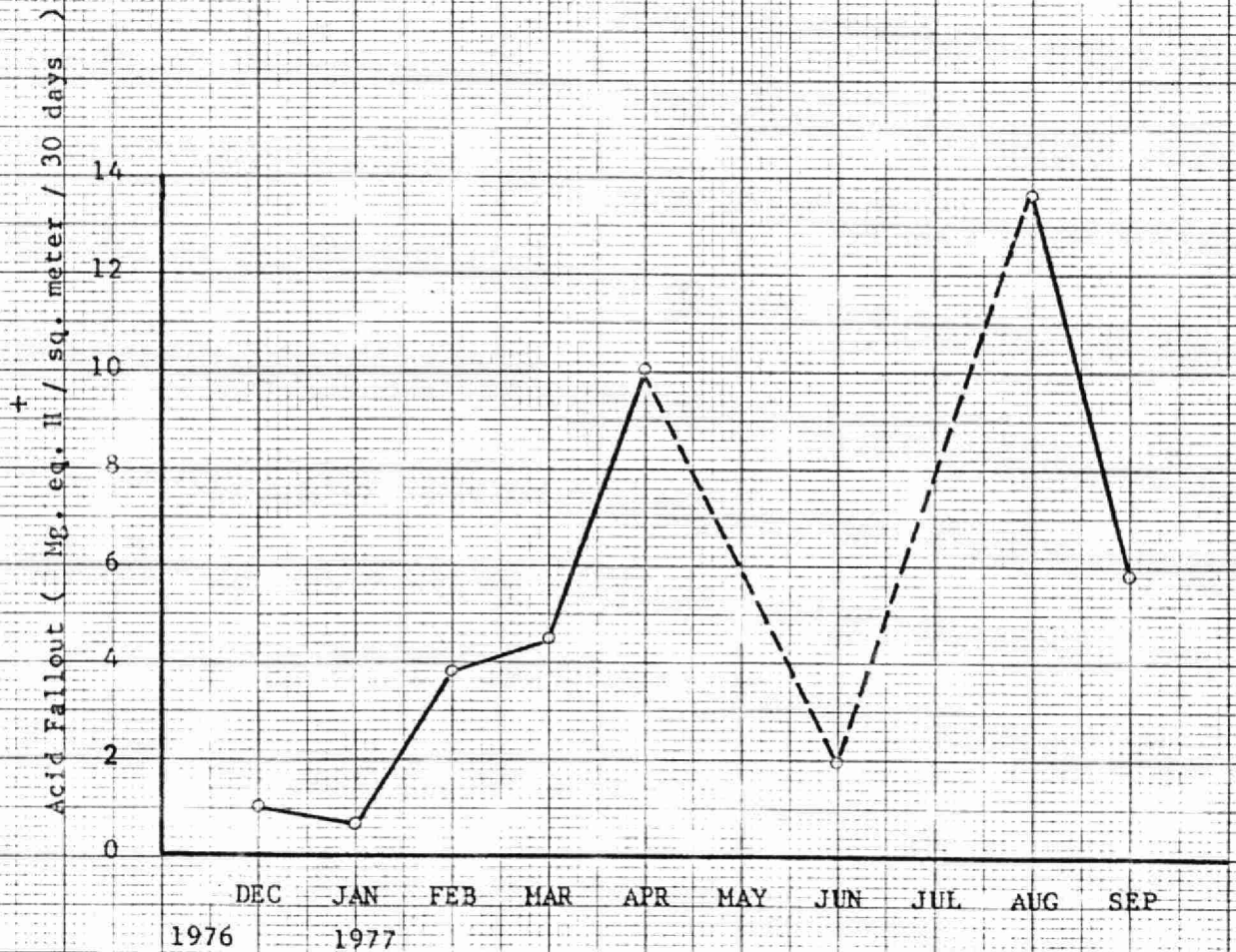
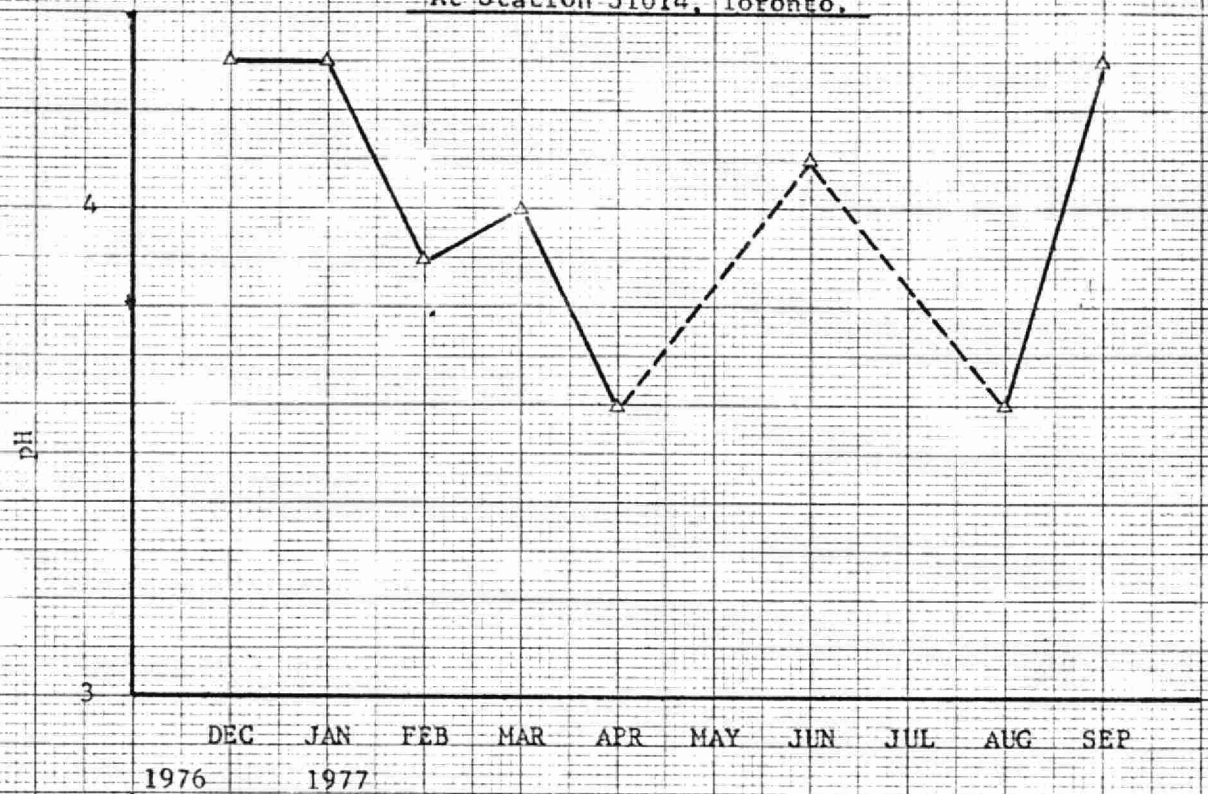
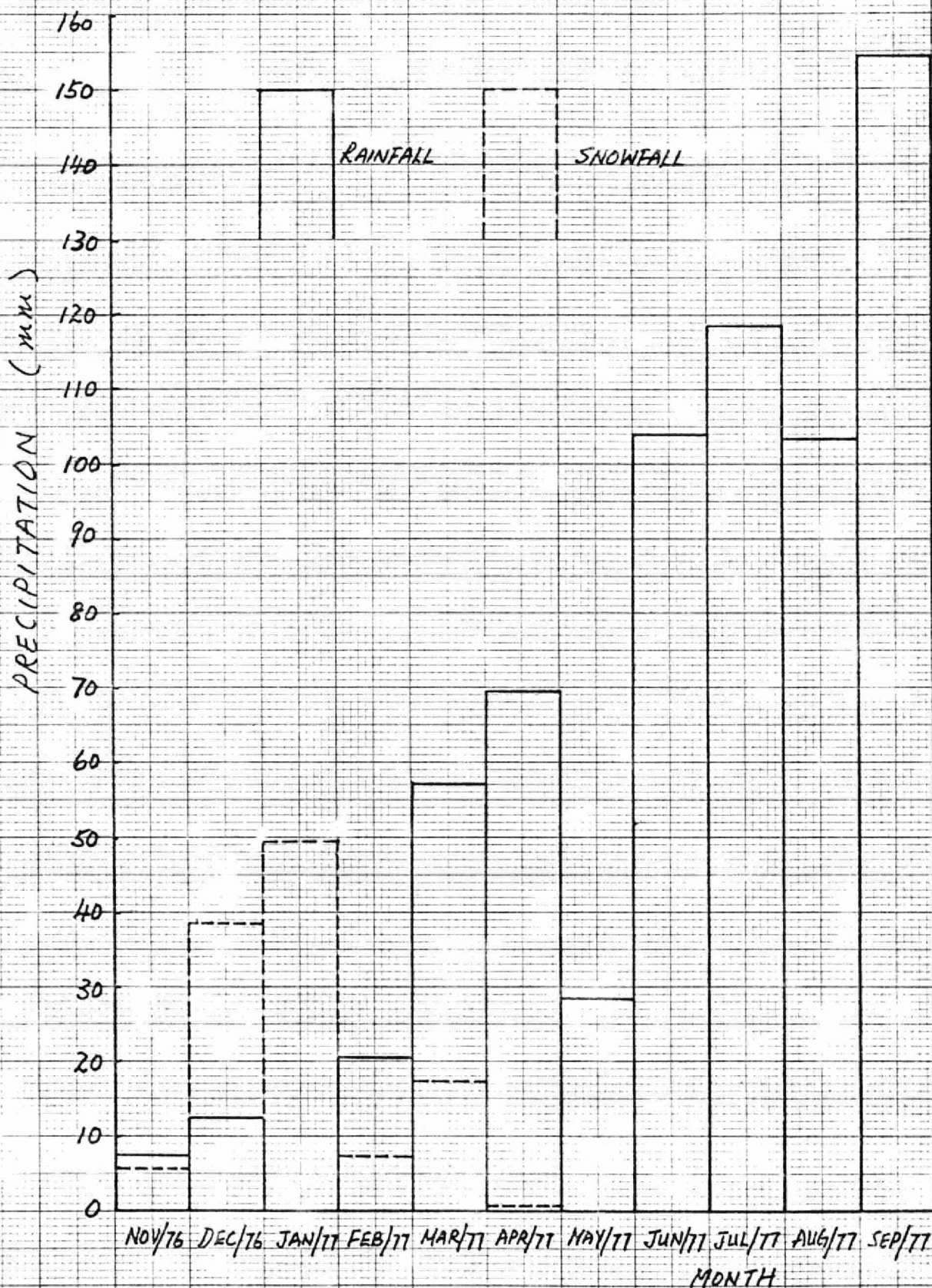


Figure 23

PRECIPITATION AT TORONTO INTERNATIONAL AIRPORT



R.Y. DEC/77

Figure 24 Seasonal Variations Of Suspended Sulphates, Sulphur Dioxide, Sulphation Rate And Ozone Concentrations At Station 31001

STATION: 31001

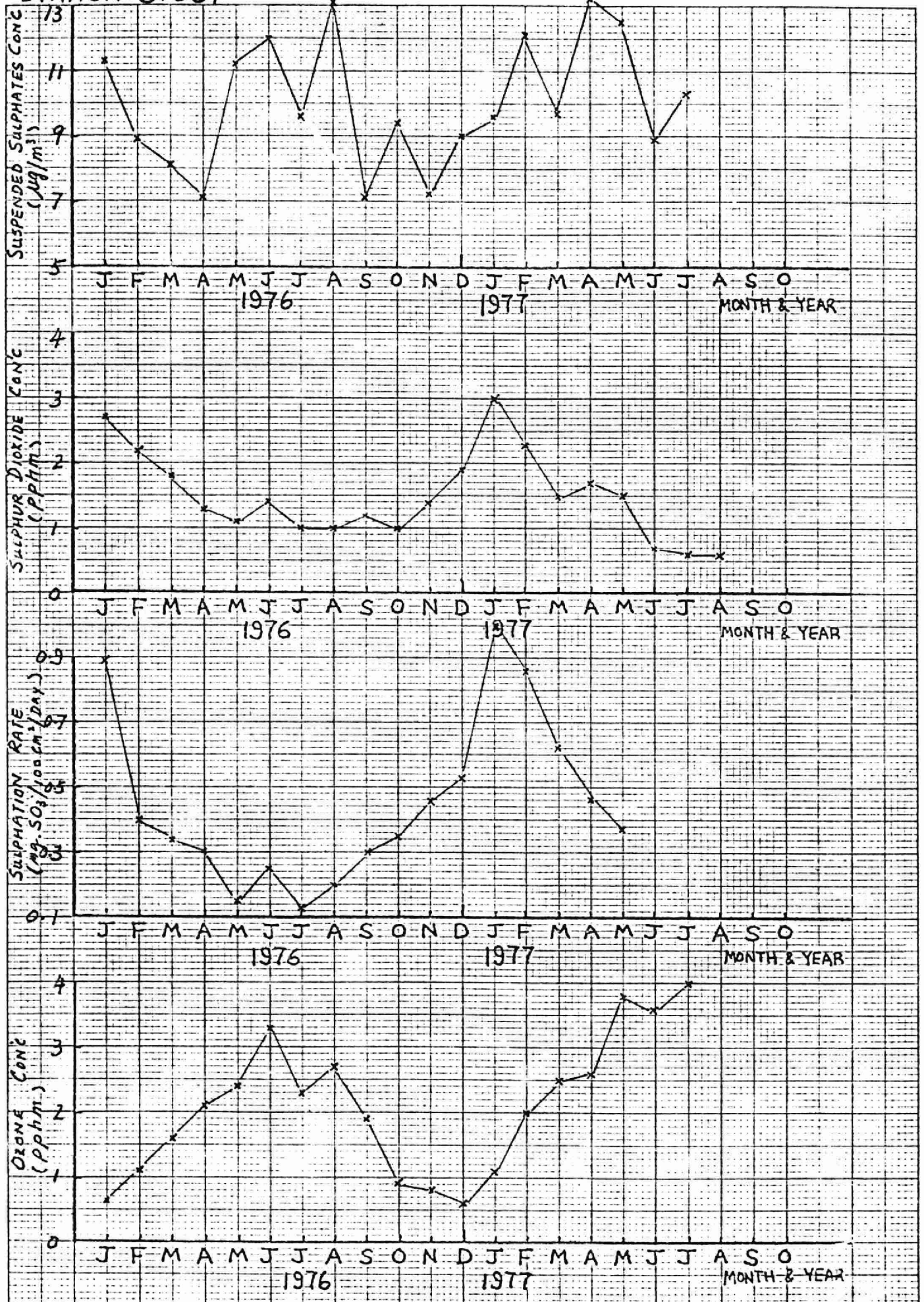
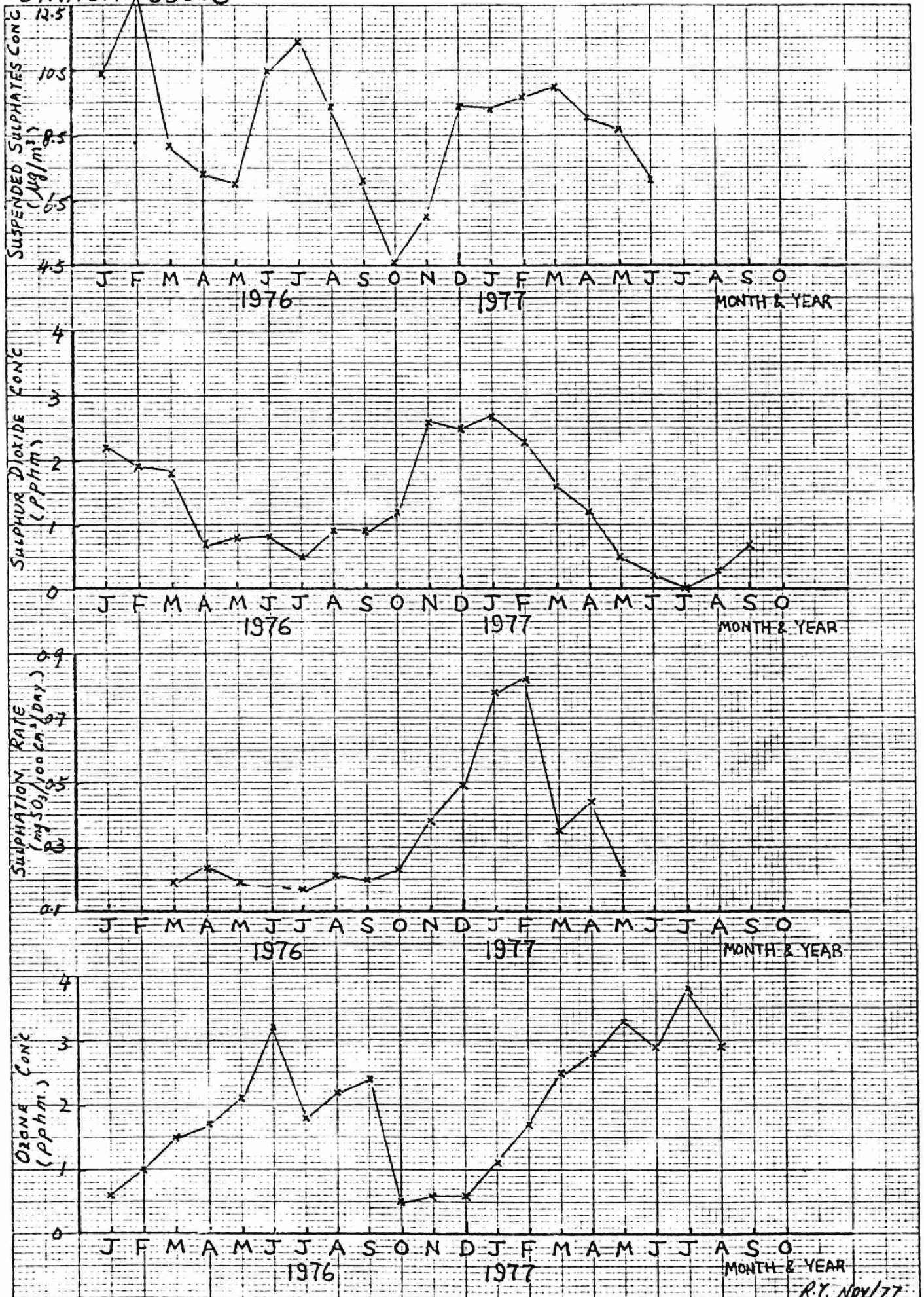


Figure 25 Seasonal Variations Of Suspended Sulphates, Sulphur Dioxide, Sulphation Rate And Ozone Concentrations At Station 33003

STATION: 33003



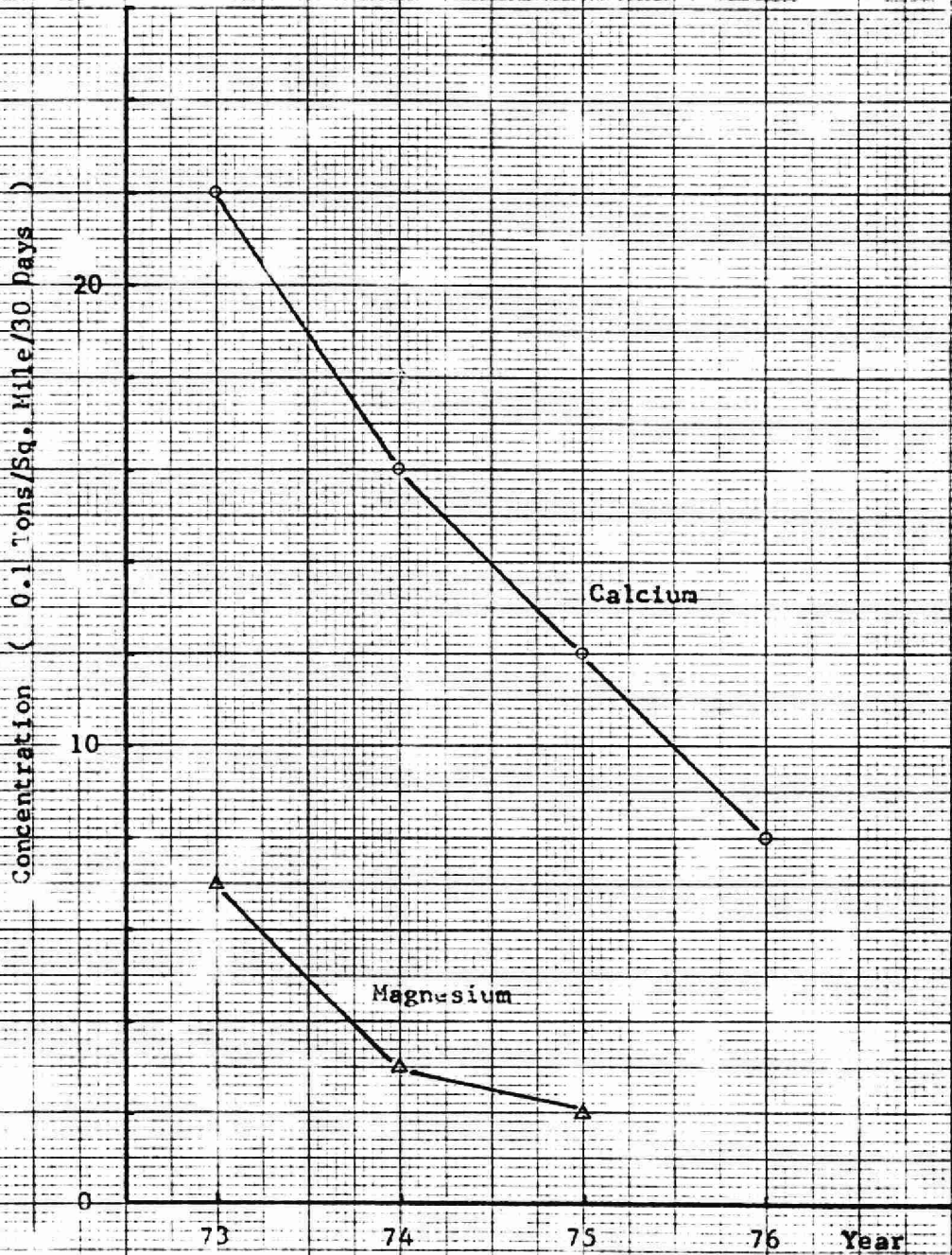
R.Y. Nov/77

46 1320

K·Σ 10 X 10 TO 1/2 INCH 7 X 10 INCHES
NEUFEL & ESSER CO. MADE IN U.S.A.

Figure 26

Annual Calcium And Magnesium In Dustfall
At Station 31001



R.Y Nov/77

Figure 27 Trends Of Suspended Particulates, Soiling Index, & Dustfall At Station 31001 (67 College St., Toronto)

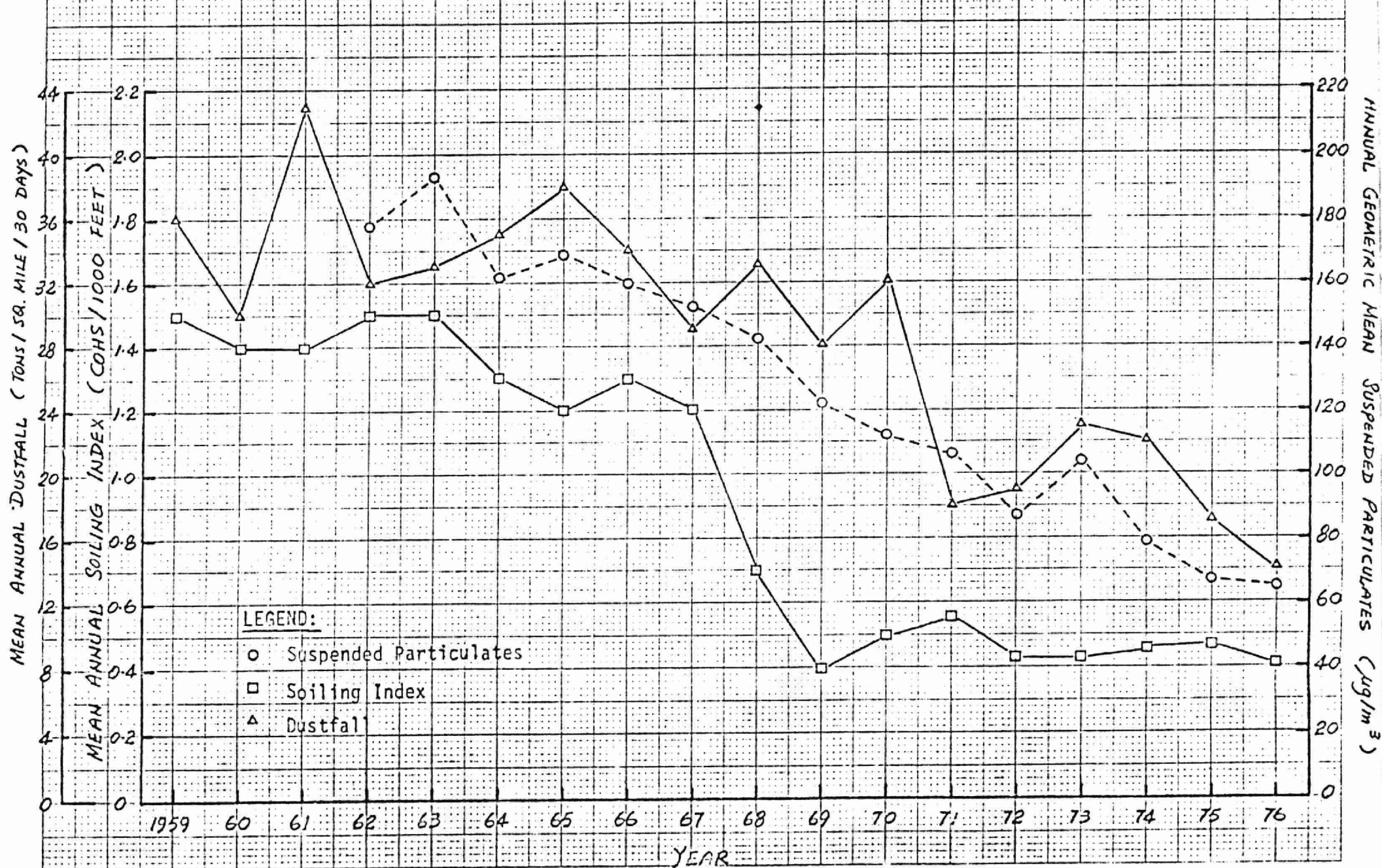


Figure 28 Changes In The Sulphate Concentrations Of
Great Lakes Waters (After Beeton, 1965).

(Reproduced From IJC Report On The Pollution
Of Lake Erie, Lake Ontario, And International
Section Of The St. Lawrence River, Vol. 1, 1969)

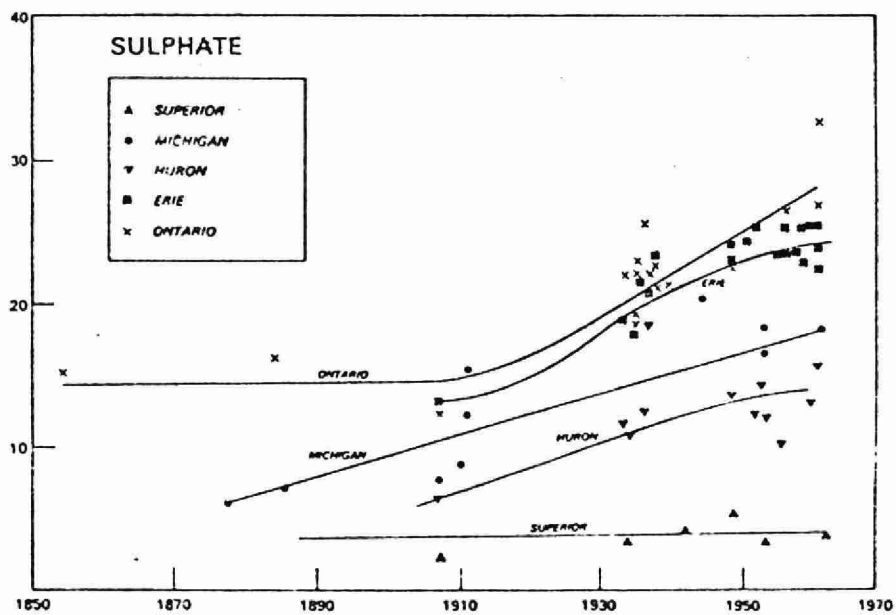
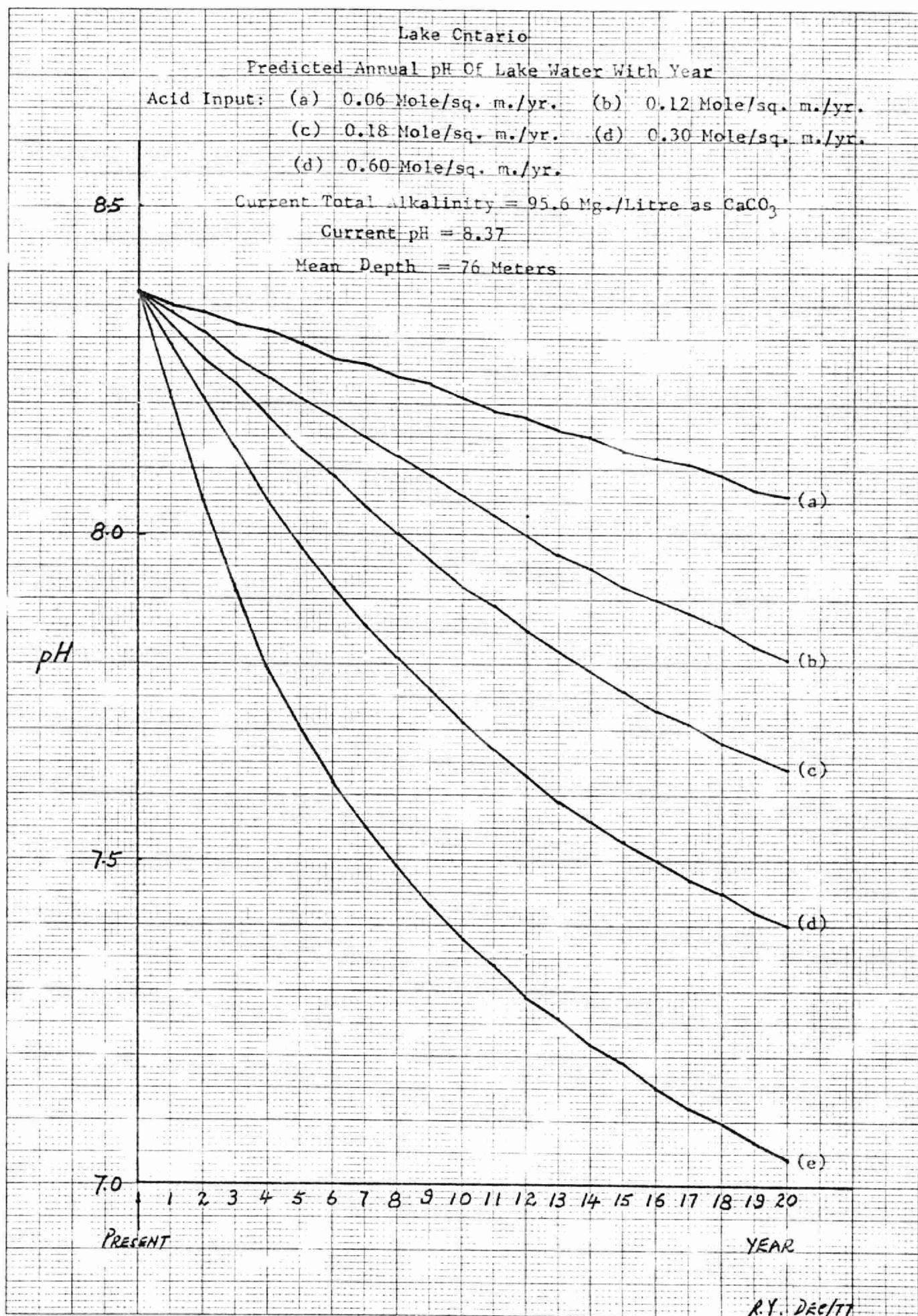


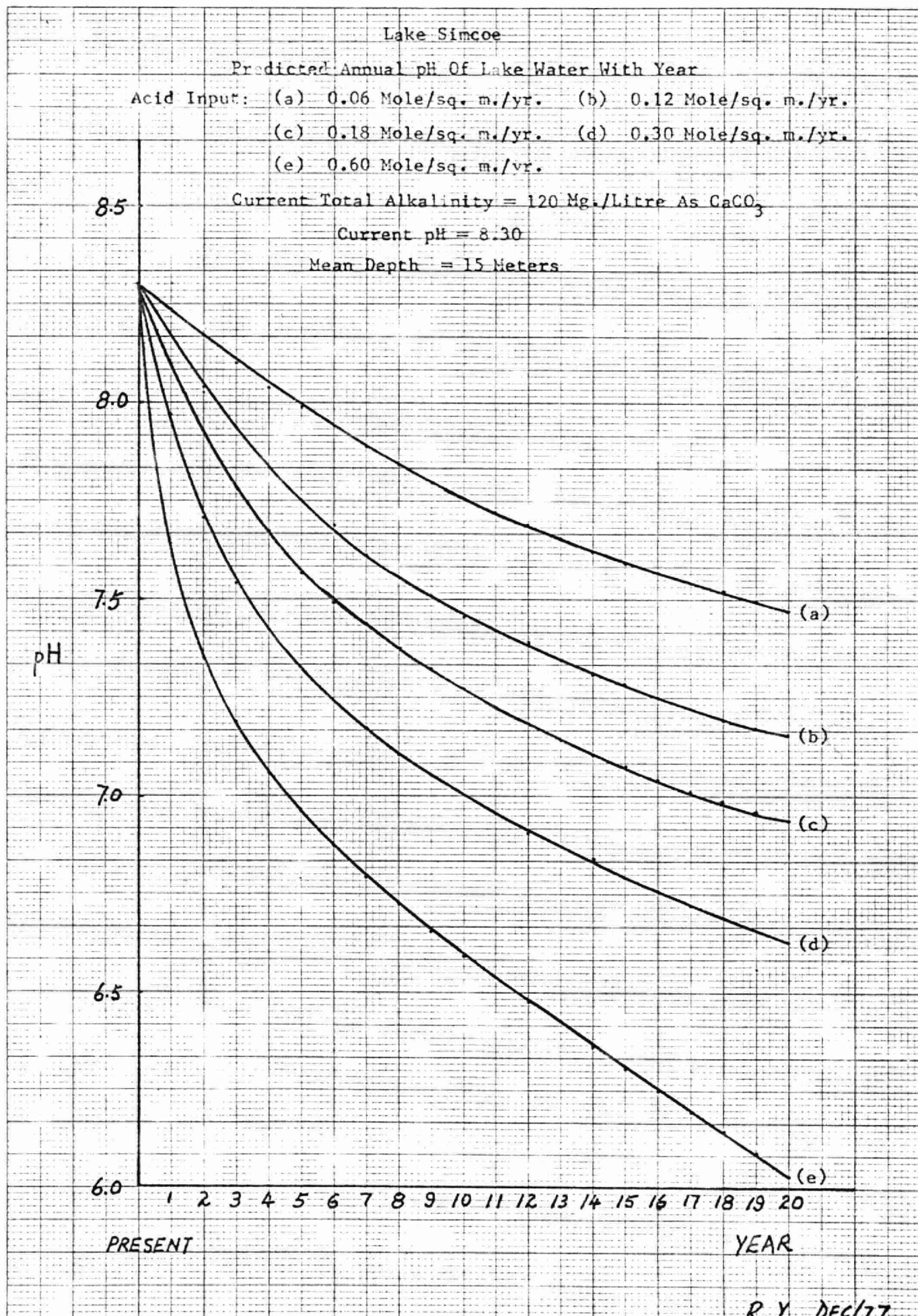
Figure 29



46 1320

10 X 10 TO 1/2 INCH 7 X 10 INCHES
 KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 30

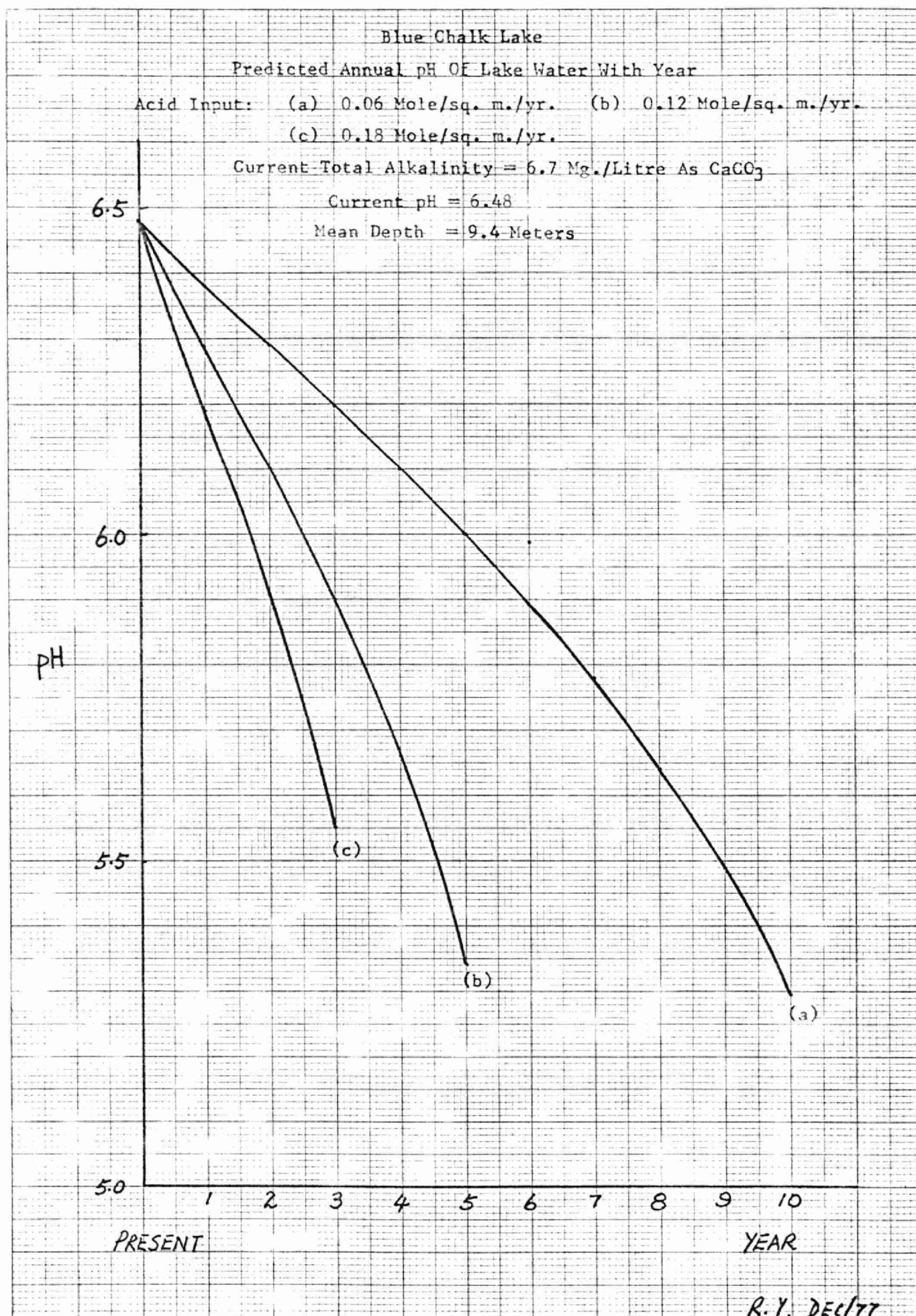


R. Y. DEC/77

46 1320

10 X 10 TO 1/2 INCH 7 X 1/2 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

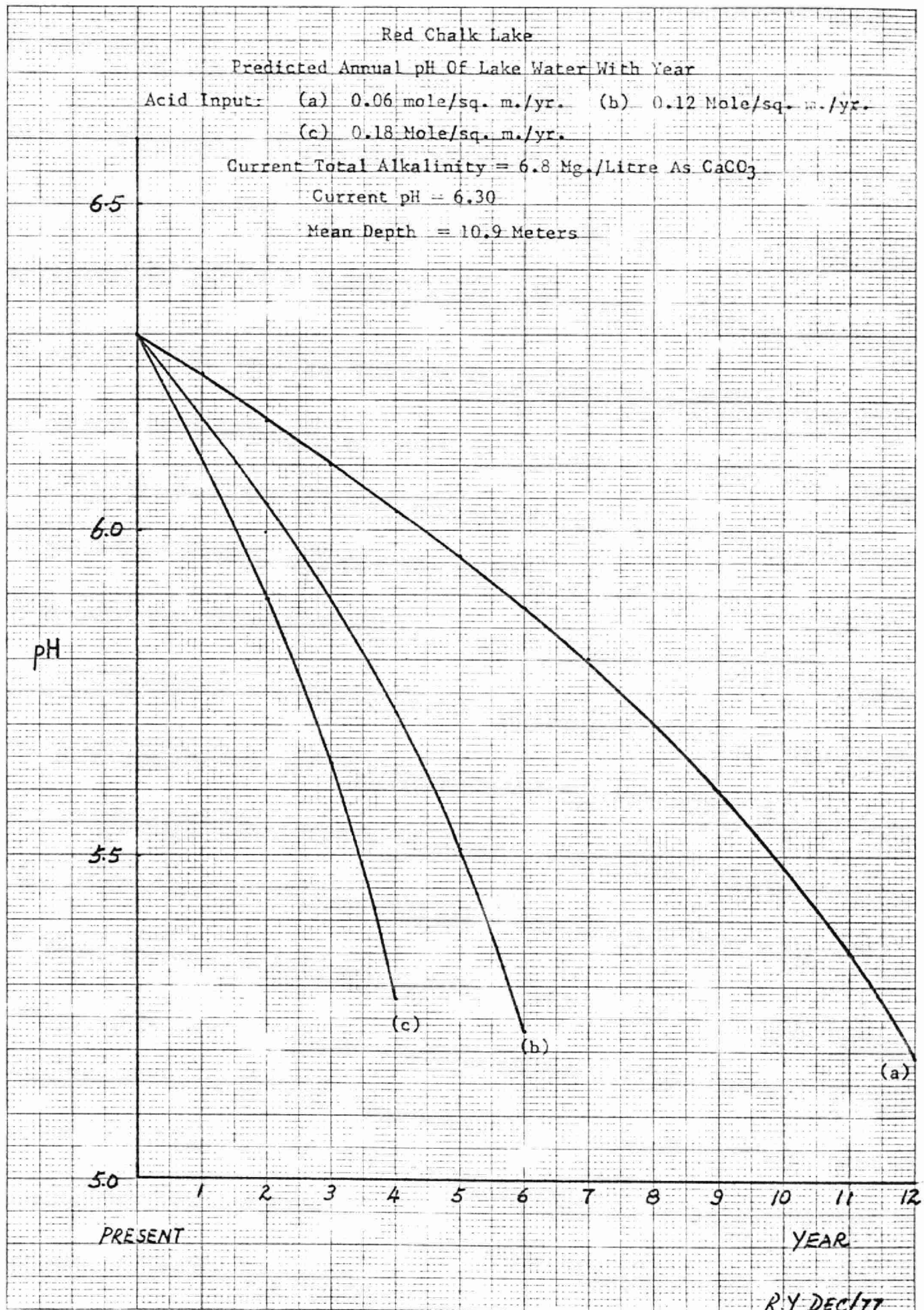
Figure 31



46 1320

10 X 10 TO 1/2 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

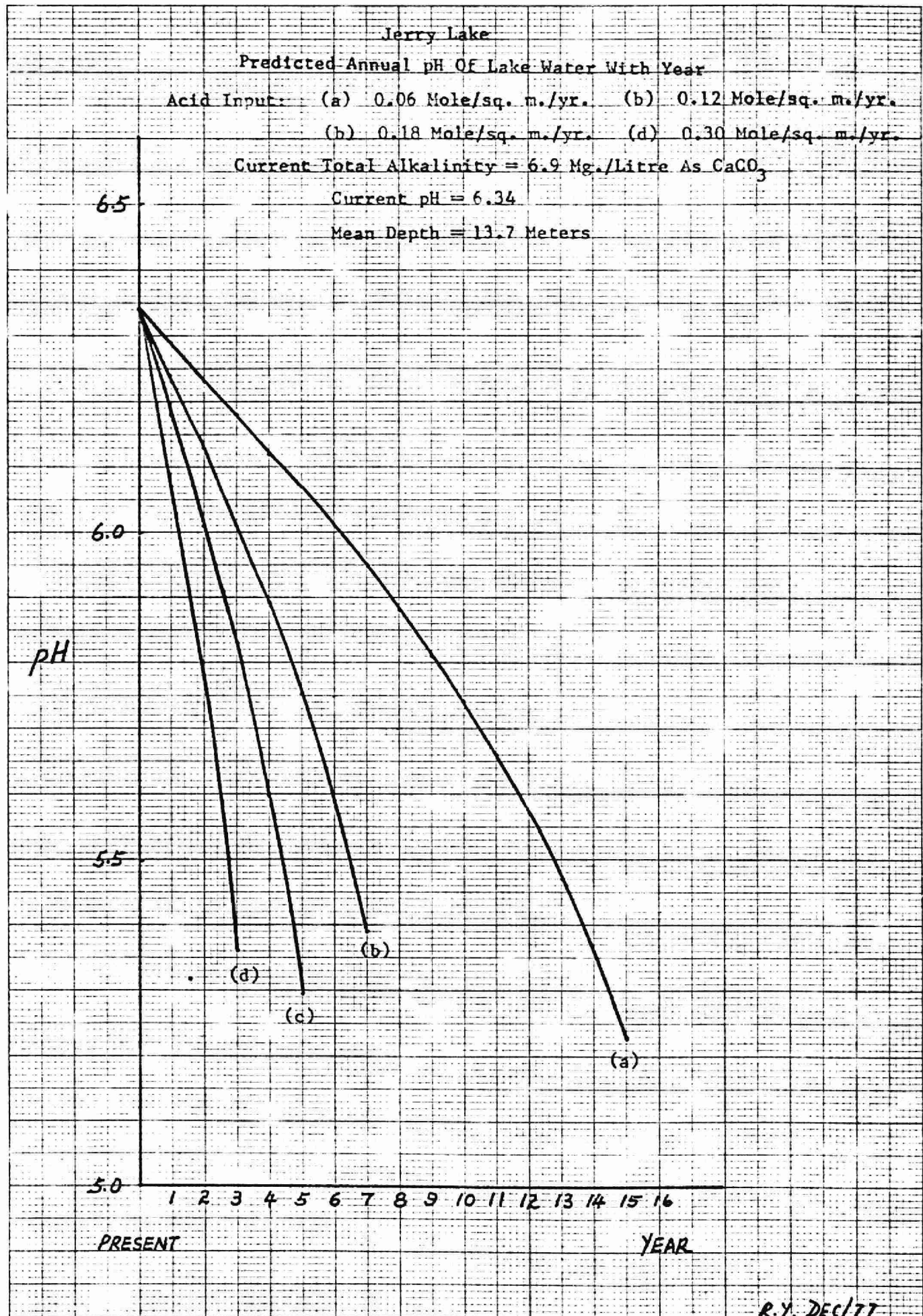
Figure 32



46 1320

KOE 10 X 10 TO 1/2 INCH 7 X 10 INCHES
KLOFFEL & ESSER CO. MADE IN USA

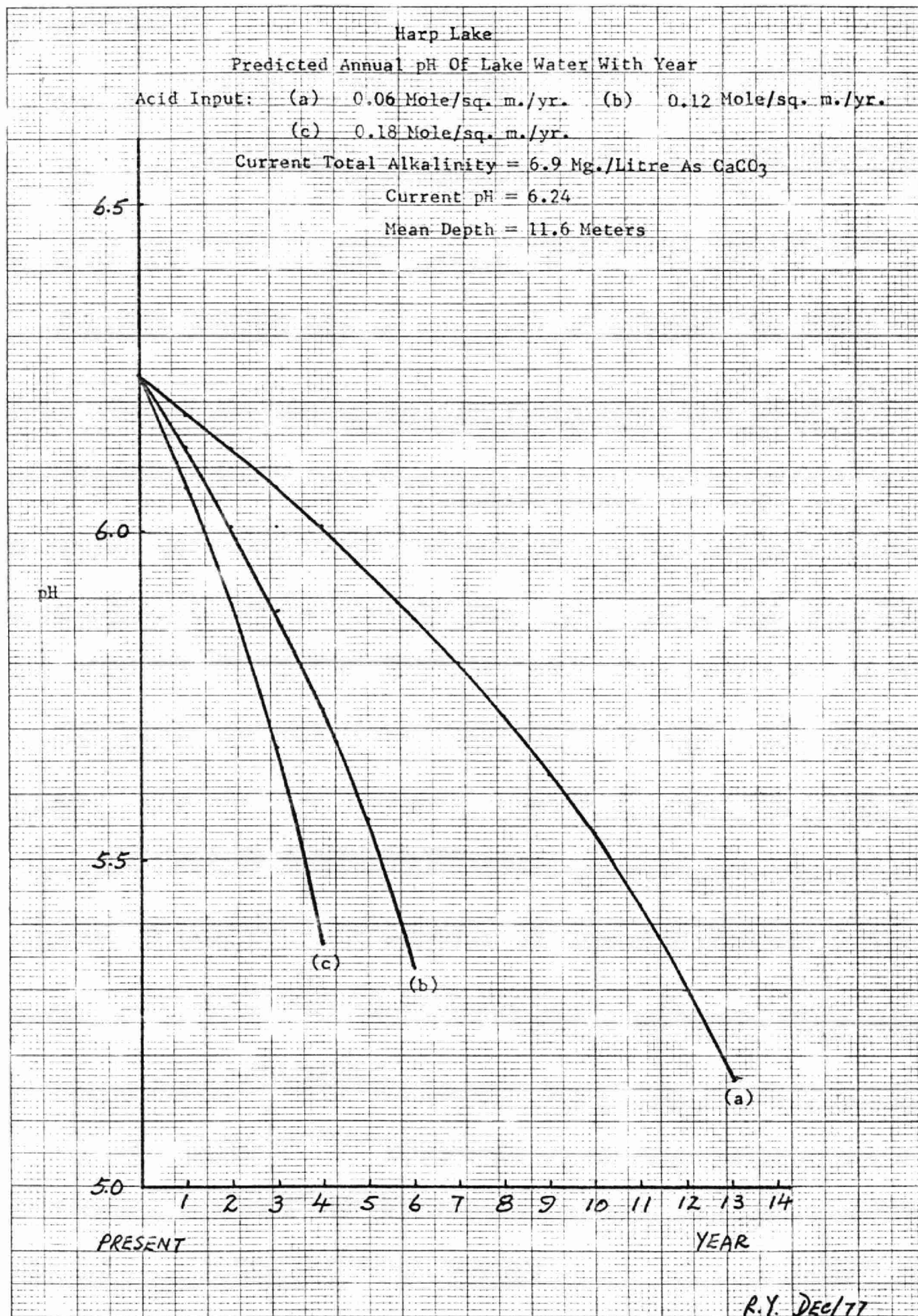
Figure 33



46 1320

K·E
 10 X 10 TO 1/2 INCH 7 X 10 INCHES
 KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 34



46 1320

K&E 10 X 10 TO 1/2 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 35

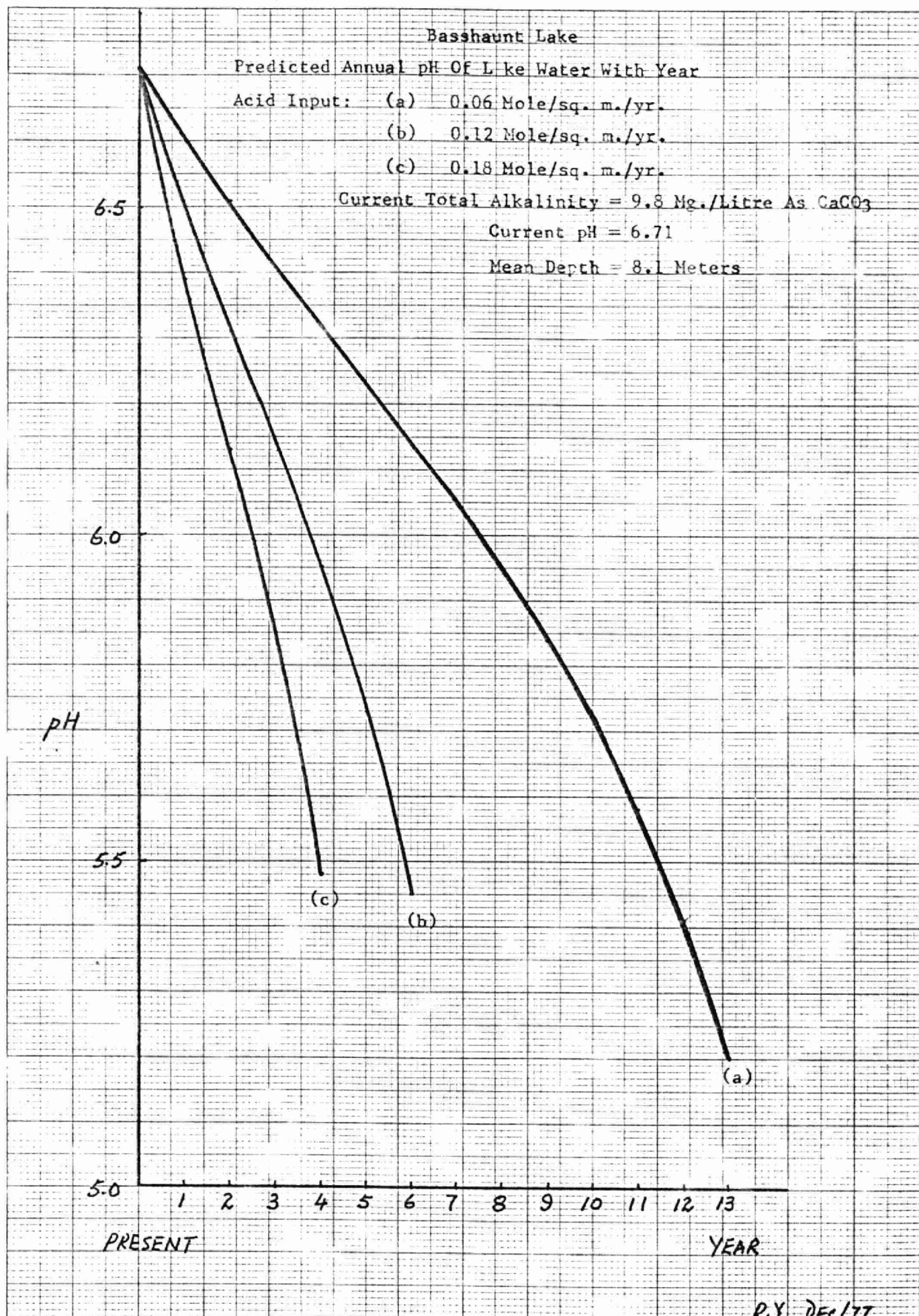
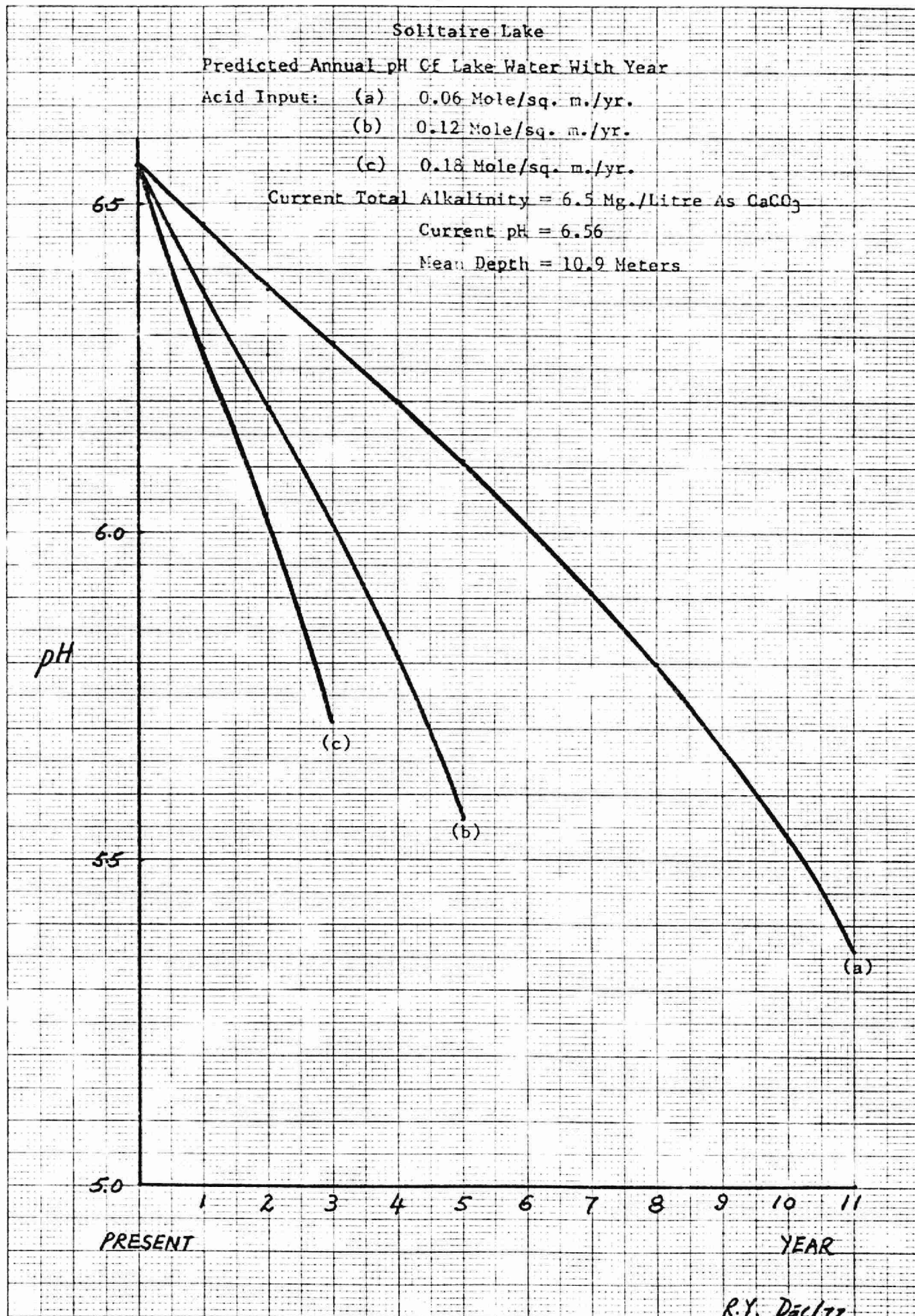


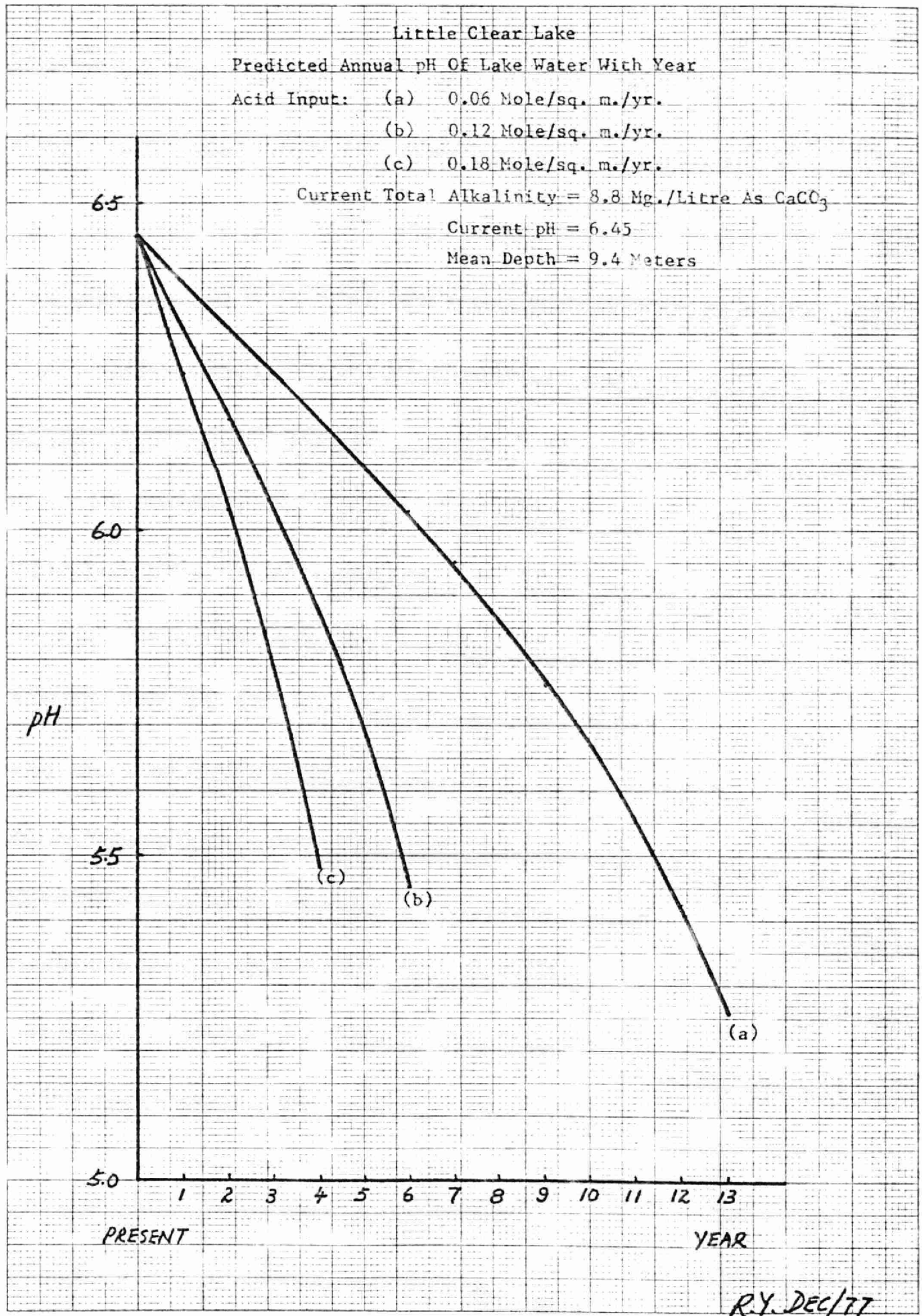
Figure 36



46 1320

10 X 10 TO 1 1/2 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

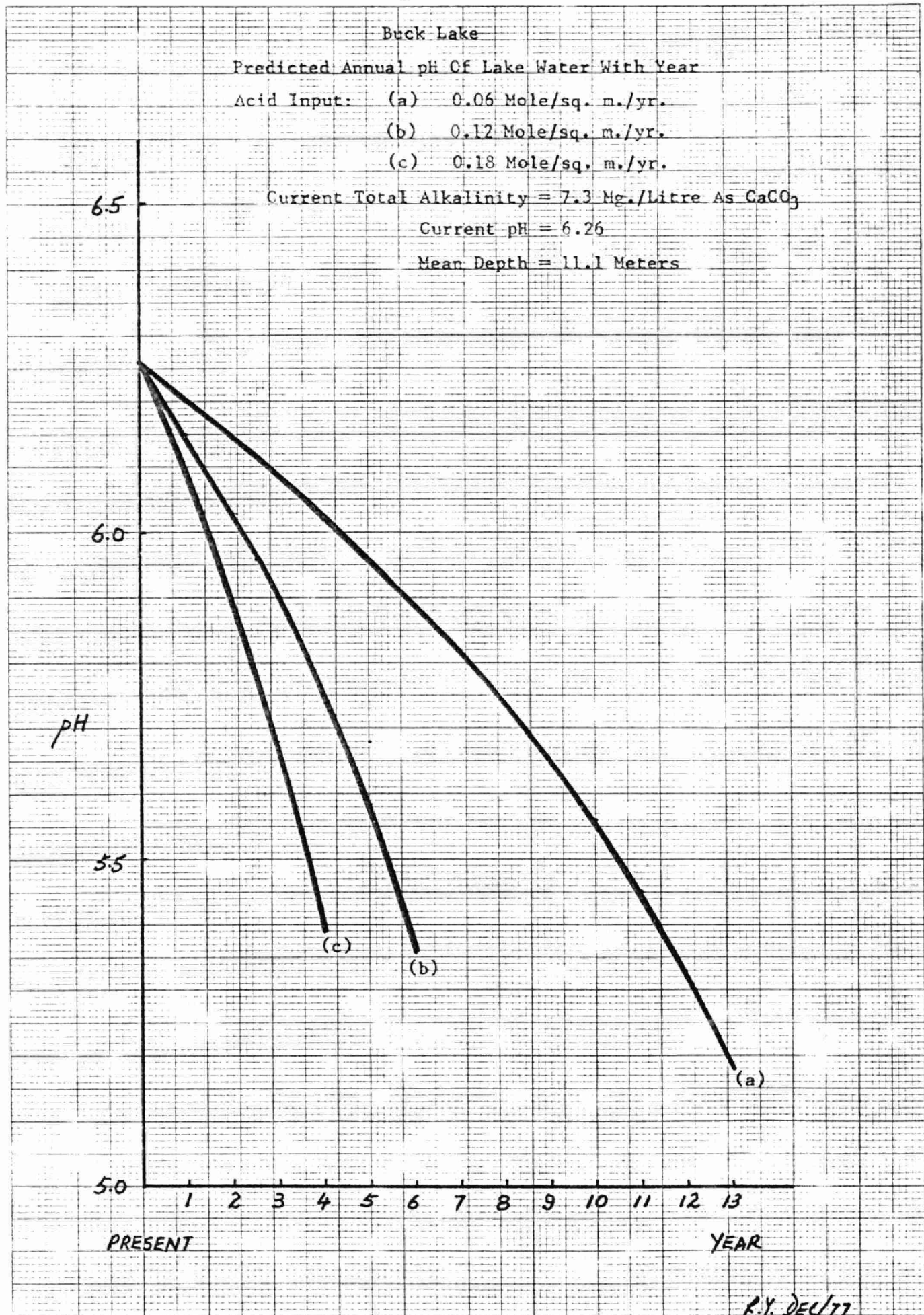
Figure 37



46 1320

K&E 10 X 10 TO 1/8 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

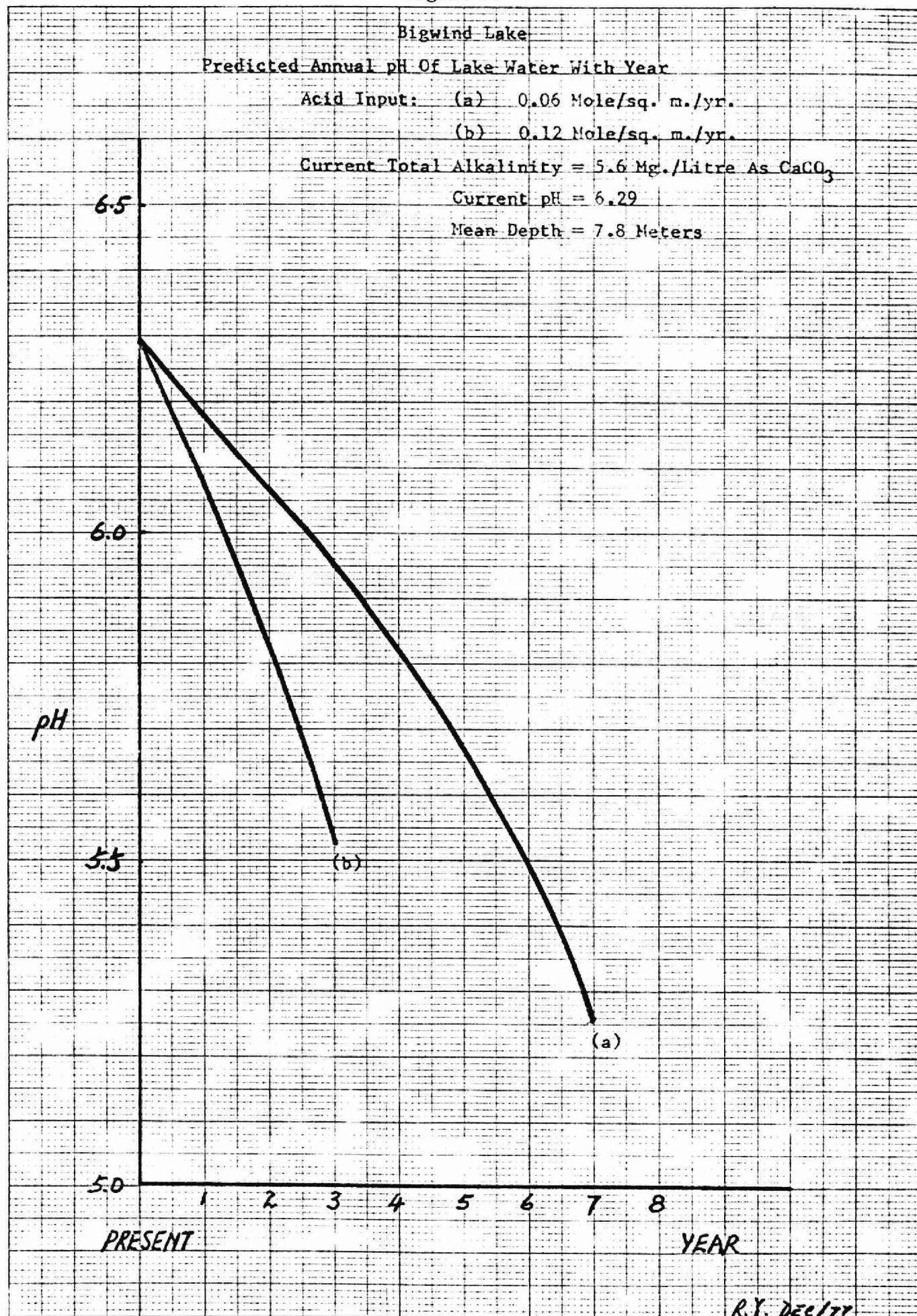
Figure 38



46 1320

10 X 10 TO 1/2 INCH 7 X 10 INCHES
 KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 39



46 1320

K&E 10 X 10 TO 1/4 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 40

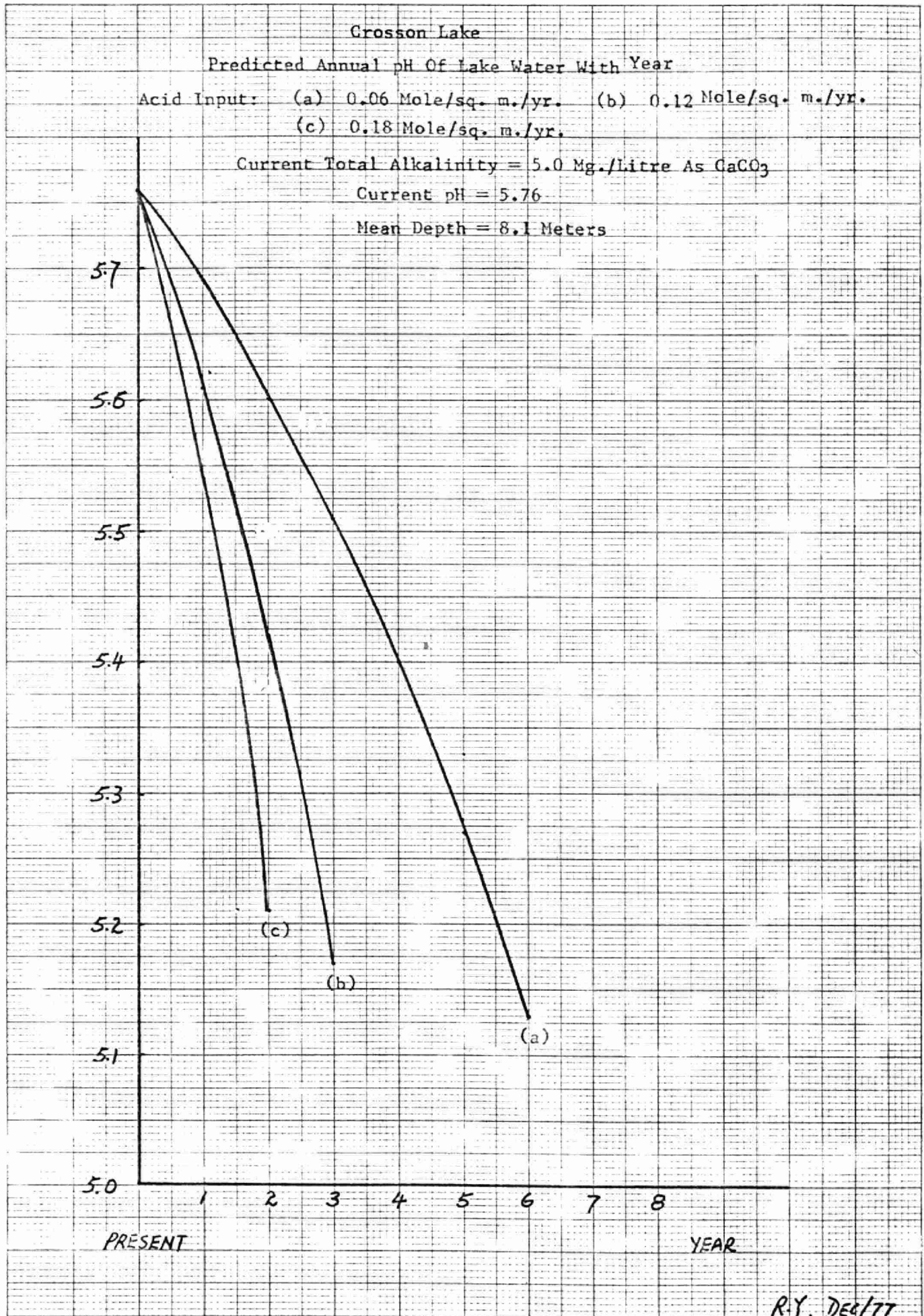
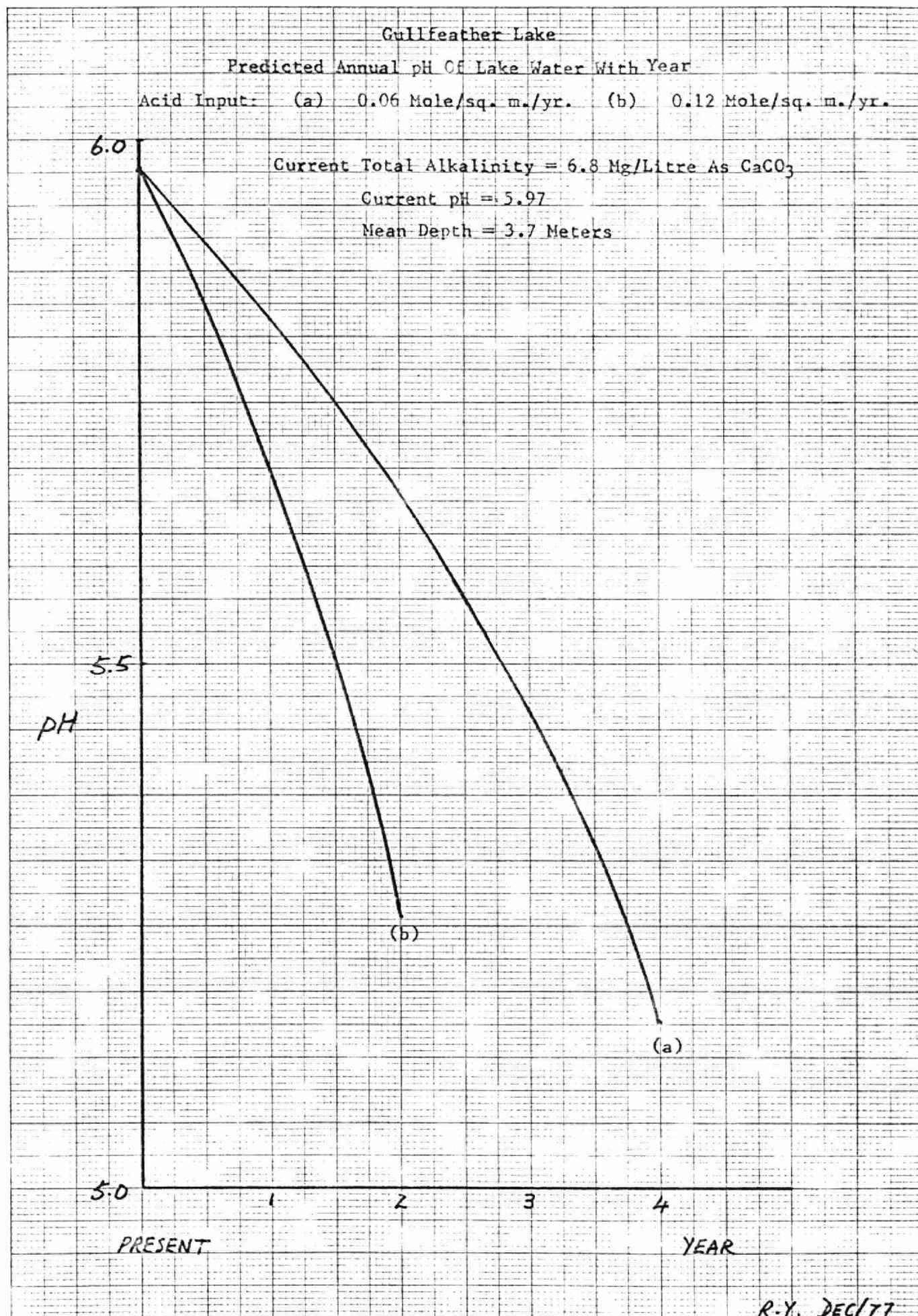


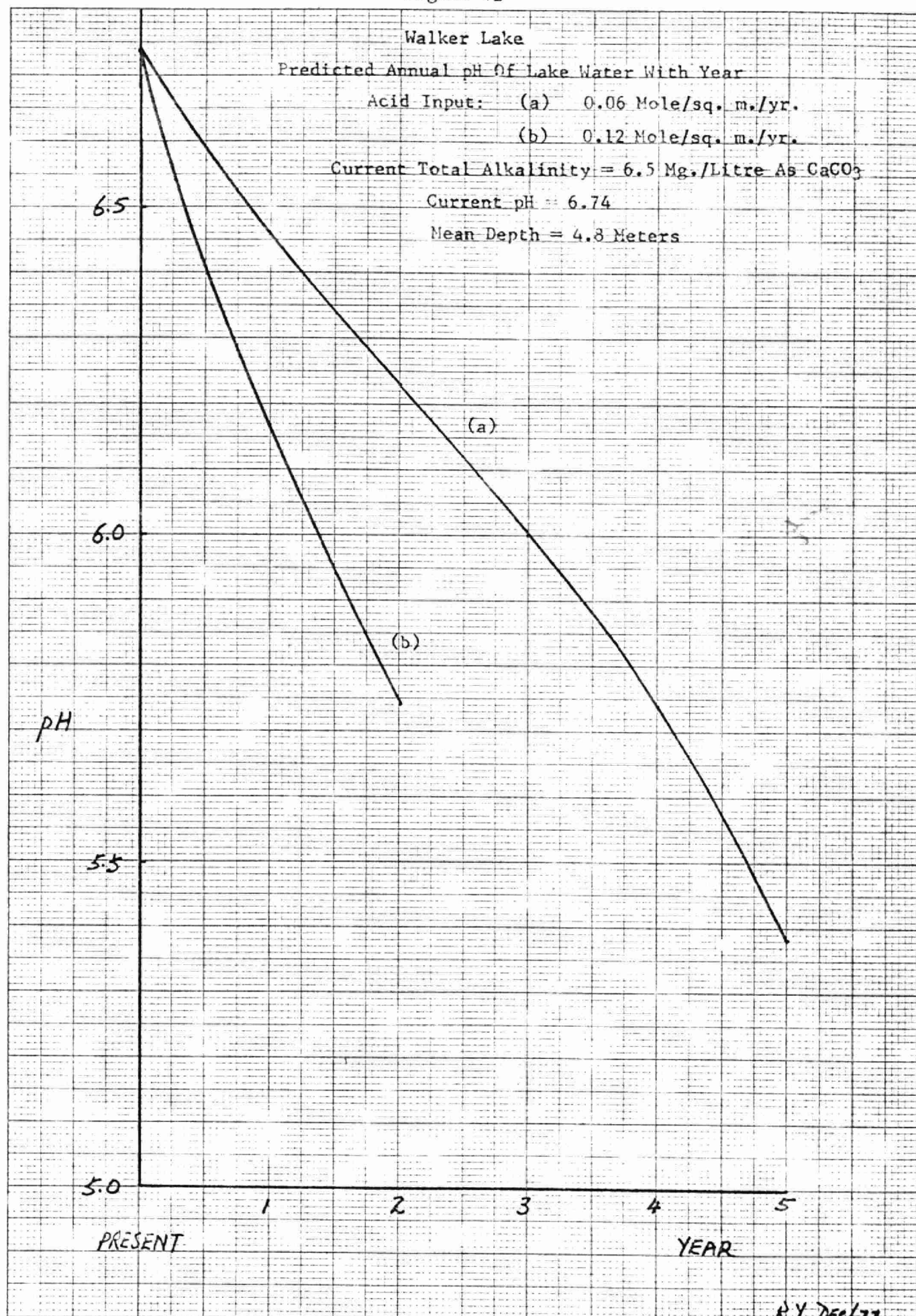
Figure 41



46 1320

K&E
10 X 10 TO 1/2 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 42



46 1320

K·Σ 10 X 10 TO 1/4 INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

Figure 43

Dickie Lake

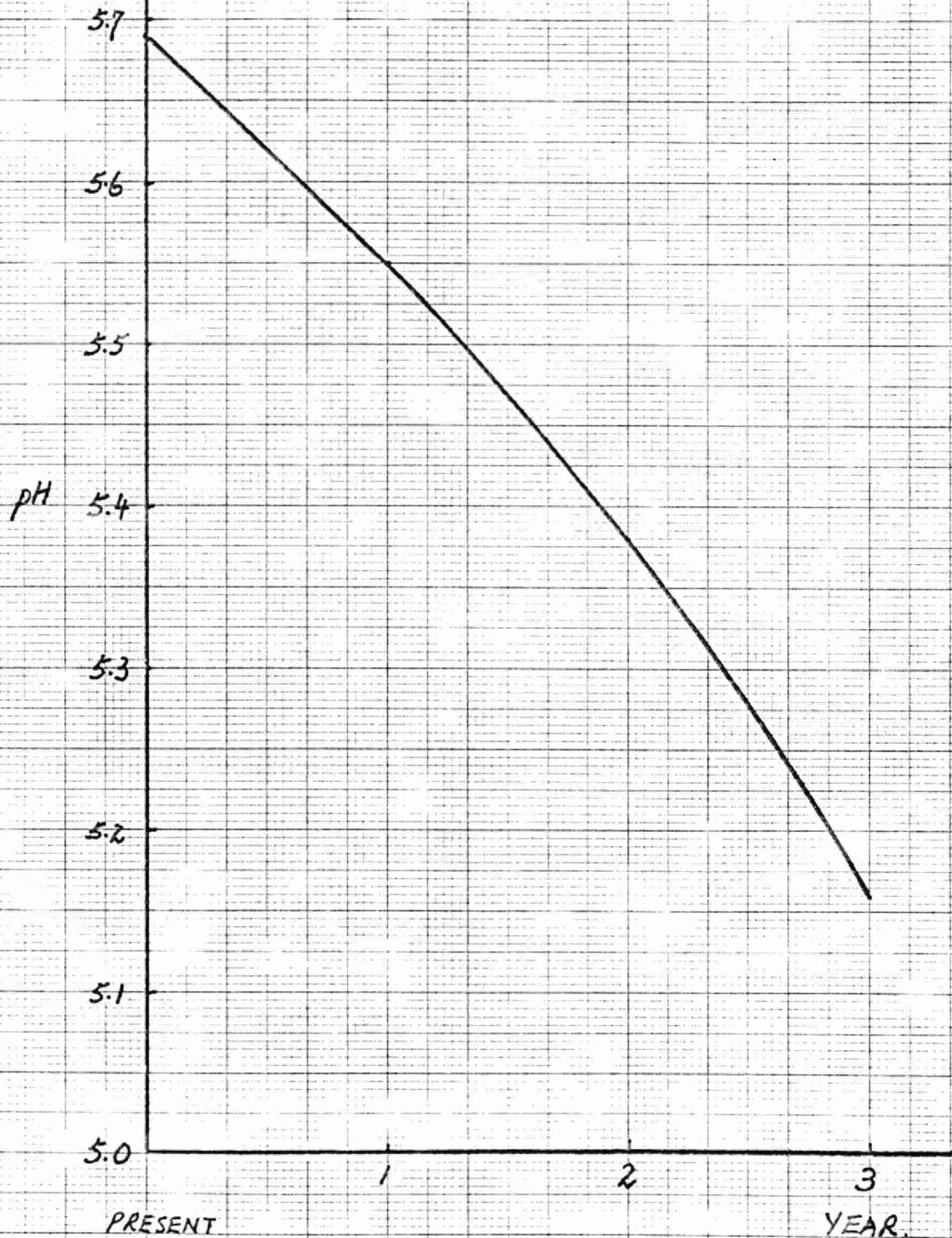
Predicted Annual pH Of Lake Water With Year

Acid Input: 0.06 Mole/sq. m./yr.

Current Total Alkalinity = 4.8 Mg./Litre As CaCO_3

Current pH = 5.69

Mean Depth = 4.4 Meters



R.Y. DEC/77

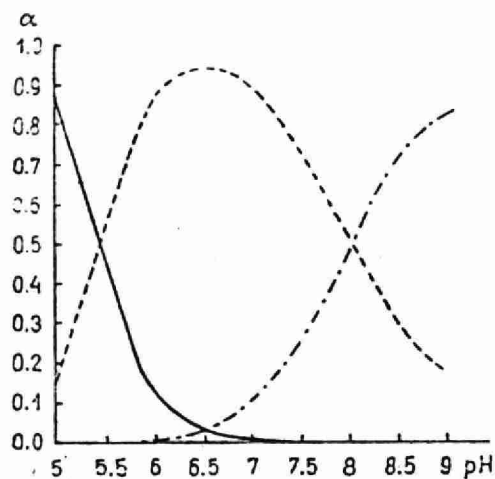


Fig. 44 Distribution of complex species in the Co(II)-histidine system as a function of pH. $T_{Co} = 5 \times 10^{-3} M$; $T_{histidine} = 1.5 \times 10^{-3} M$; $\beta^1 = 1.98 \times 10^7$; $\beta_2 = 4.11 \times 10^{11}$; $K_1'' = 10^{-4}$; $K_2'' = 6.76 \times 10^{-10}$; — $\alpha_{Co^{2+}}$ - - - α_{CoL^+} - · - α_{CoL_2}

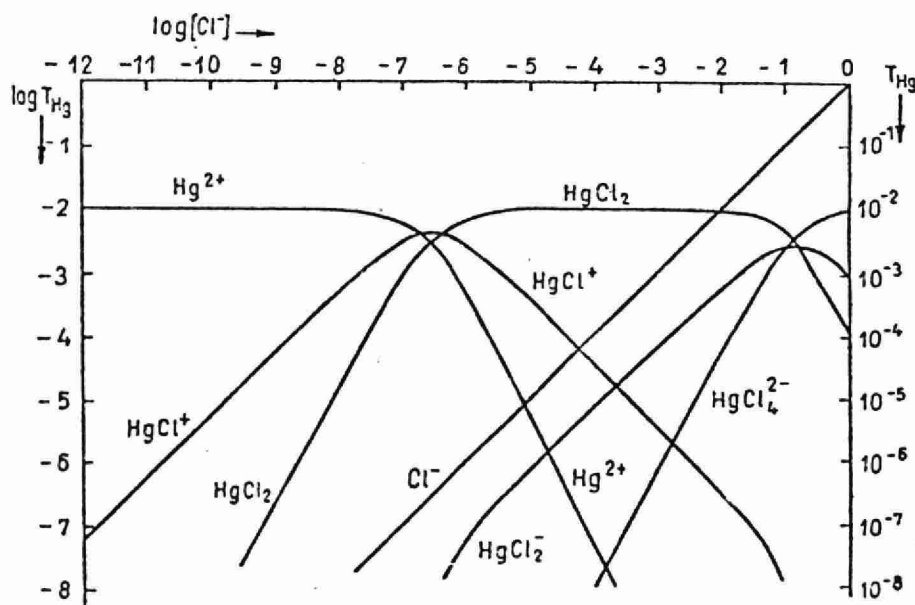


Fig. 45 Logarithmic diagram for $T_{Hg} = 0.01 M$ and varying $[Cl^-]$, showing the concentrations of the different species.

(Reproduced From M. T. Beck, "Chemistry Of Complex Equilibria".)

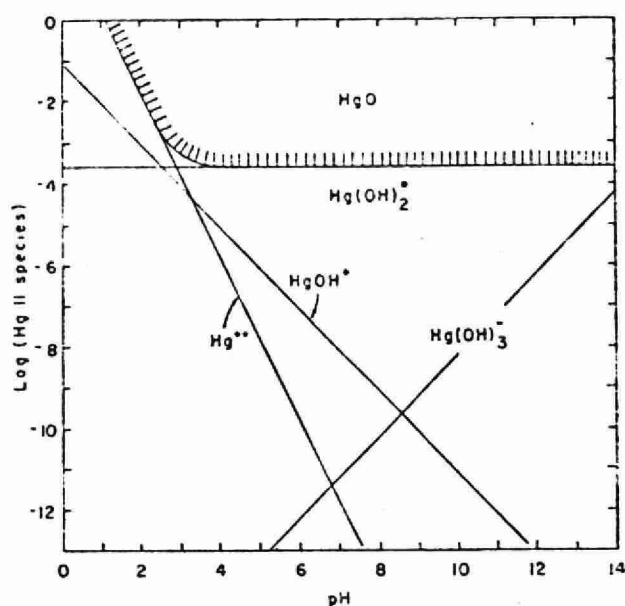


Figure 46 Log concentration-pH solubility diagram for HgO in aqueous solution at 25°C .

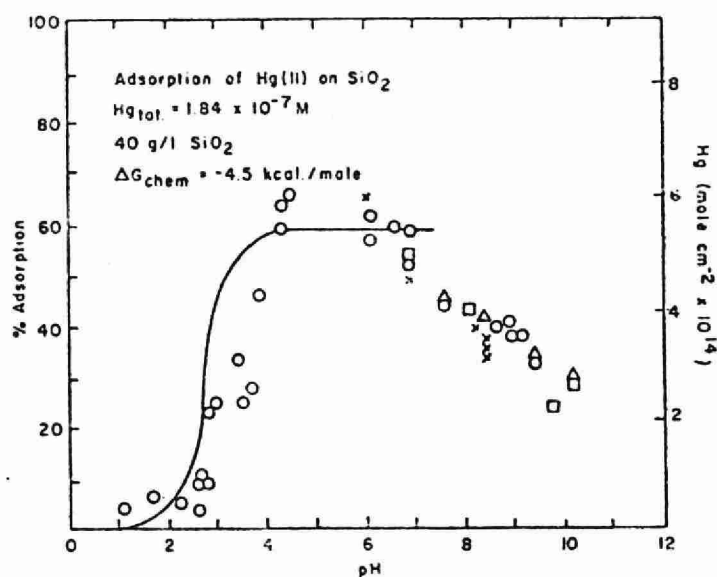
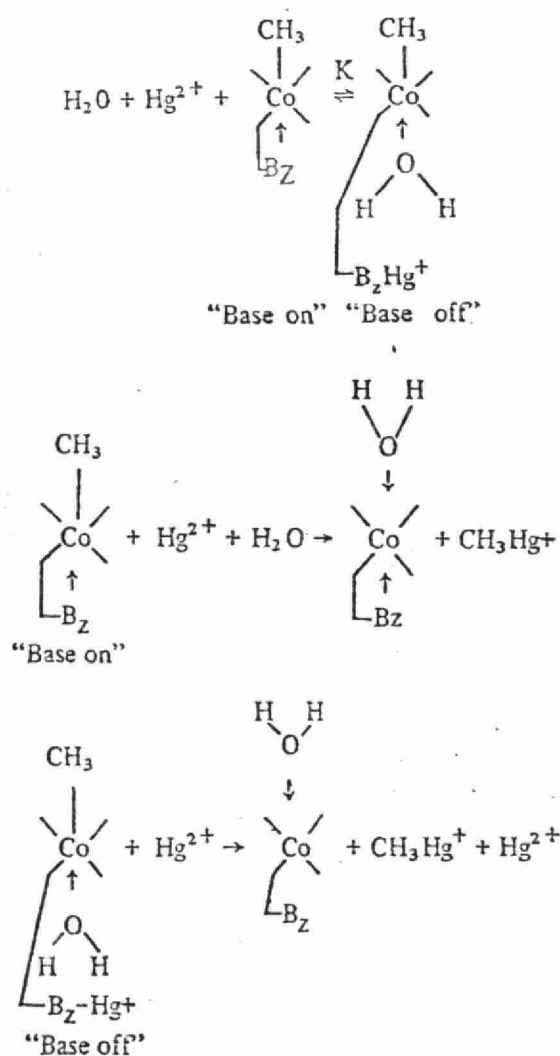
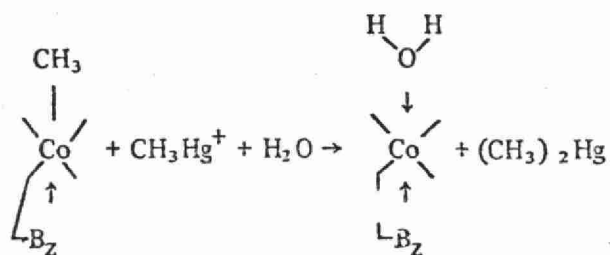


Figure 47 Experimental adsorption isotherms for Hg(II) from $1.84 \times 10^{-7} \text{ M}$ solutions by quartz as a function of pH and ionic strength. The ionic strength conditions are $10^{-1} \text{ M NaClO}_4$, $1 \times 10^{-2} \text{ M NaClO}_4$, $2 \times 10^{-3} \text{ M NaClO}_4$, $1 \times 10^{-1} \text{ M Mg(NO}_3)_2$.

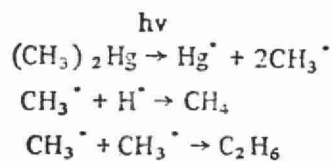
(Reproduced From A.J. Rubin, "Aqueous-Environmental Chemsitry Of Metals.)



The biosynthesis of methylmercury.



The biosynthesis of dimethylmercury.



The photolysis of dimethylmercury.

Figure 48 Mechanisms For The Formation Of Methylmercury And Dimethylmercury.



96936000119903

TABLES DE CONVERSION AU SYSTEME METRIQUE

POUCES EN MILLIMÈTRES									
po.	mm	po.	mm	po.	mm	po.	mm	po.	mm
10	254.000	1	25.400	0.1	2.540	0.01	0.254	0.001	0.025
20	508.000	2	50.800	0.2	5.080	0.02	0.508	0.002	0.051
30	762.000	3	76.200	0.3	7.620	0.03	0.762	0.003	0.076
40	1,016.000	4	101.600	0.4	10.160	0.04	1.016	0.004	0.102
50	1,270.000	5	127.000	0.5	12.700	0.05	1.270	0.005	0.127
60	1,524.000	6	152.400	0.6	15.240	0.06	1.524	0.006	0.152
70	1,778.000	7	177.800	0.7	17.780	0.07	1.778	0.007	0.178
80	2,032.000	8	203.200	0.8	20.320	0.08	2.032	0.008	0.203
90	2,286.000	9	228.600	0.9	22.860	0.09	2.286	0.009	0.229
100	2,540.000	10	254.000	1.0	25.400	0.10	2.540	0.010	0.254

MILLIMÈTRES EN POUCES									
mm	po.	mm	po.	mm	po.	mm	po.	mm	po.
100	3.9370	10	0.3937	1	0.0394	0.1	0.0039	0.01	0.0003
200	7.8740	20	0.7874	2	0.0787	0.2	0.0079	0.02	0.0007
300	11.8110	30	1.1811	3	0.1181	0.3	0.0118	0.03	0.0011
400	15.7480	40	1.5748	4	0.1575	0.4	0.0157	0.04	0.0015
500	19.6850	50	1.9685	5	0.1968	0.5	0.0197	0.05	0.0019
600	23.6220	60	2.3622	6	0.2362	0.6	0.0236	0.06	0.0023
700	27.5590	70	2.7559	7	0.2756	0.7	0.0276	0.07	0.0027
800	31.4960	80	3.1496	8	0.3150	0.8	0.0315	0.08	0.0031
900	35.4330	90	3.5433	9	0.3543	0.9	0.0354	0.09	0.0035
1,000	39.3701	100	3.9370	10	0.3937	1.0	0.0394	0.10	0.0039

FRACTIONS DE POUCE EN MILLIMÈTRES									
po.	mm	po.	mm	po.	mm	po.	mm	po.	mm
$\frac{1}{16}$	0.397	$\frac{1}{8}$	3.175	$\frac{1}{4}$	6.350	$\frac{3}{8}$	9.525	$\frac{1}{2}$	12.700
$\frac{1}{8}$	0.794	$\frac{3}{16}$	4.763	$\frac{1}{4}$	6.350	$\frac{5}{16}$	7.938	$\frac{3}{8}$	9.525
$\frac{3}{16}$	1.191	$\frac{1}{4}$	6.350	$\frac{5}{16}$	7.938	$\frac{3}{8}$	9.525	$\frac{1}{2}$	12.700
$\frac{1}{4}$	1.588	$\frac{3}{8}$	9.525	$\frac{1}{2}$	12.700	$\frac{5}{8}$	15.875	$\frac{3}{4}$	19.050
$\frac{5}{8}$	1.588	$\frac{3}{8}$	9.525	$\frac{1}{2}$	12.700	$\frac{5}{8}$	15.875	$\frac{3}{4}$	19.050
$\frac{3}{4}$	1.984	$\frac{1}{2}$	12.700	$\frac{5}{8}$	15.875	$\frac{3}{4}$	19.050	$\frac{7}{8}$	22.225
$\frac{7}{8}$	2.381	$\frac{3}{4}$	19.050	$\frac{7}{8}$	22.225	$\frac{15}{16}$	23.813	$\frac{15}{16}$	23.813
$\frac{15}{16}$	2.381	$\frac{3}{4}$	19.050	$\frac{7}{8}$	22.225	$\frac{15}{16}$	23.813	$\frac{15}{16}$	23.813
$\frac{1}{2}$	12.700	$\frac{3}{4}$	19.050	$\frac{7}{8}$	22.225	$\frac{15}{16}$	23.813	$\frac{15}{16}$	23.813

PIEDS EN MILLIMÈTRES									
pi.	mm	pi.	mm	pi.	mm	pi.	mm	pi.	mm
100	30,480	10	3,048	1	304,8	0.1	30,48	0.01	3,048
200	60,960	20	6,096	2	609,6	0.2	60,96	0.02	6,096
300	91,440	30	9,144	3	914,4	0.3	91,44	0.03	9,144
400	121,920	40	12,192	4	1,219,2	0.4	121,92	0.04	12,192
500	152,400	50	15,240	5	1,524,0	0.5	152,40	0.05	15,240
600	182,880	60	18,288	6	1,828,8	0.6	182,88	0.06	18,288
700	213,360	70	21,336	7	2,133,6	0.7	213,36	0.07	21,336
800	243,840	80	24,384	8	2,438,4	0.8	243,84	0.08	24,384
900	274,320	90	27,432	9	2,743,2	0.9	274,32	0.09	27,432
1,000	304,800	100	30,480	10	3,048,0	1.0	304,80	0.10	30,480

PIEDS EN MÈTRES (1 pi. = 0.3048 m)									
pi.	mètres	pi.	mètres	pi.	mètres	pi.	mètres	pi.	mètres
100	30.480	10	3.048	1	0.305	0.1	0.305	0.01	0.030
200	60.960	20	6.096	2	0.610	0.2	0.610	0.02	0.061
300	91.440	30	9.144	3	0.914	0.3	0.914	0.03	0.091
400	121.920	40	12.192	4	1.219	0.4	1.219	0.04	0.122
500	152.400	50	15.240	5	1.524	0.5	1.524	0.05	0.152
600	182.880	60	18.288	6	1.829	0.6	1.829	0.06	0.183
700	213.360	70	21.336	7	2.134	0.7	2.134	0.07	0.213
800	243.840	80	24.384	8	2.438	0.8	2.438	0.08	0.244
900	274.320	90	27.432	9	2.743	0.9	2.743	0.09	0.274
1,000	304.800	100	30.480	10	3.048	1.0	3.048	0.10	0.305

MÈTRES EN PIÈDES (m = 3.28033 pi.)									
mètres	pi.	mètres	pi.	mètres	pi.	mètres	pi.	mètres	pi.
1	3.281	0.1	0.328	0.01	0.032	0.001	0.003	0.0001	0.0003
2	6.562	0.2	0.656	0.02	0.066	0.002	0.006	0.0002	0.0006
3	9.843	0.3	0.984	0.03	0.098	0.003	0.009	0.0003	0.0009
4	13.123	0.4	1.312	0.04	0.131	0.004	0.013	0.0004	0.0013
5	16.404	0.5	1.640	0.05	0.164	0.005	0.016	0.0005	0.0016
6	19.685	0.6	1.968	0.06	0.197	0.006	0.019	0.0006	0.0019
7	22.966	0.7	2.297	0.07	0.230	0.007	0.023	0.0007	0.0023
8	26.247	0.8	2.625	0.08	0.262	0.008	0.026	0.0008	0.0026
9	29.528	0.9	2.953	0.09	0.295	0.009	0.295	0.0009	0.295
10	32.808	1.0	3.281	0.10	0.328	0.010	0.328	0.0010	0.328

MILLES EN KILO (1 mille = 1.609 km)									
milles	km	milles	km	milles	km	milles	km	milles	km
1,000	1,609.35	100	160.93	10	16.09	1	1.609	0.1	0.161
2,000	3,218.69	200	321.87	20	32.18	2	3.219	0.2	0.322
3,000	4,828.04	300	482.80	30	48.28	3	4.829	0.3	0.483
4,000	6,437.39	400	643.74	40	64.37	4	6.437	0.4	0.644
5,000	8,046.74	500	804.67	50	80.47	5	8.047	0.5	0.805
6,000	9,656.08	600	965.61	60	96.56	6	9.656	0.6	0.966
7,000	11,265.43	700	1,126.54	70	112.65	7	11.265	0.7	1.127
8,000	12,874.78	800	1,287.48	80	128.75	8	12.875	0.8	1.288
9,000	14,484.12	900	1,448.41	90	144.84	9	14.484	0.9	1.449
10,000	16,093.47	1,000	1,609.35	100	160.93	10	16.093	0.10	1.610

KILOMÈTRES EN MILES (= 0.621370 mille)									
km	milles	km	milles	km	milles	km	milles	km	milles
10	6.21	1	0.62	0.1	0.062	0.01	0.006	0.001	0.0006
20	12.43	2	1.24	0.2	0.124	0.02	0.012	0.002	0.0012
30	18.64	3	1.86	0.3	0.186	0.03	0.018	0.003	0.0018
40	24.86	4	2.49	0.4	0.249	0.04	0.025	0.004	0.0025
50	31.07	5	3.11	0.5	0.311	0.05	0.031	0.005	0.0031
60	37.28	6	3.73	0.6	0.373	0.06	0.037	0.006	0.0037
70	43.50	7	4.35	0.7	0.435	0.07	0.043	0.007	0.0043
80	49.71	8	4.97	0.8	0.497	0.08	0.050	0.008	0.0050
90	55.92	9	5.59	0.9	0.559	0.09	0.056	0.009	0.0056
100	62.14	10	6.21	1.0	0.62	0.10	0.062	0.010	0.0062

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1 GRAMME	=	1,000	MILLIGRAMME
1 KILOGRAMME	=	1,000	GRAMME
1 TONNE MÉTRIQUE	=	1,000	KILOGRAMME
1 GRAIN	=	0.0648	GRAMME
1 ONCE	=	28.35	GRAMME
1 LIVRE	=	453.6	GRAMME
1 TONNE	=	907.2	KILOGRAMME

TEMPÉRATURE

CELSIUS	FAHRENHEIT
-273.2	= -459.7
-40	= -40
-17.7	= 0
0	= +32
+37	= +98.6
+100	= +212

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